

C13.2:R31/7



Research Activities

INORGANIC MATERIALS DIVISION

**Center for Materials Science
National Measurement Laboratory
National Bureau of Standards**

Fall 1983



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PREFACE

This report is an informal summary of the Research Activities of the Inorganic Materials Division, U.S. National Bureau of Standards during fiscal year 1983. The information contained herein was taken in part from the 1982 Annual Report of the Center for Materials Science, NBSIR 83-2783. This document, however, is not an official publication of the National Bureau of Standards. It describes work in progress, and it is not intended that it be referenced in open literature citations. Information regarding the technical work is available from the investigators cited or from:

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I. INTRODUCTION

The mission of the Inorganic Materials Division is to provide industry, government agencies, and scientific organizations with data, measurement methods, standards, reference materials, and fundamental concepts related to processing, structure, chemistry, physical properties, and performance of ceramics, glasses, and other inorganic materials. The Division pursues studies of inorganic materials to foster their safe, efficient, and economical use, and to address national concerns for productivity, critical materials, and environmental quality.

Advanced ceramic materials currently account for a ten billion dollar market worldwide in electronic, dielectric, structural, and other applications. Prospective new applications such as ceramic components for high-temperature, fuel-efficient heat engines offer the prospect of greatly expanded market opportunities for the US ceramic industry. The major roadblocks to expanded high-technology applications of advanced ceramic materials is their inherently brittle nature and the inability of current technology to produce consistently defect-free ceramic components with acceptable service life and reproducible properties. The key to improved reliability of ceramics is the elimination of microstructural defects, and the key to defect-free microstructure is improved understanding and control of processing.

During Fiscal Year 1983, the Inorganic Materials Division has restructured its activities to give increased emphasis to research underlying ceramic processing and performance in response to the needs of industry and other government agencies for basic data and concepts supporting advanced ceramics technology. New or expanded programs have been developed in ceramic phase diagrams, ceramic powder processing, characterization of microstructure evolution during processing, non-destructive evaluation of green state ceramics, and the mechanical properties of ceramics under service conditions. In addition, the Division has maintained programs in other areas of materials processing and performance, including unique activities in biocorrosion and bioprocessing of metals, tribology (including friction and wear of advanced ceramic materials), and completion of the NBS recycled oil program.

Critically evaluated reference data required for processing and use of inorganic materials is an important Division output. The Phase Diagrams for Ceramists Data Center compiles, evaluates, and disseminates ceramic phase diagrams in close cooperation with the American Ceramic Society (ACerS). A formal agreement was concluded with ACerS during the past year that establishes an accelerated program, under NBS technical leadership, to provide timely evaluated phase diagrams to the ceramic community. The Division has expanded its work on phase diagram modeling, improved thermochemical evaluation techniques for phase diagrams, and the development of a computerized ceramic phase diagram data base, while ACerS has initiated a major development program to raise four million dollars from industry to provide expanded phase diagram dissemination services such as on-line availability of phase diagram information. This program is closely integrated with the activities of the NBS/American Society for Metals Alloy Phase Diagram Data Center to ensure efficient use of resources in areas of common concern such as the development of computer graphics.

A somewhat similar cooperative program with the Joint Committee on Powder Diffraction Standards/International Centre for Diffraction Data (JCPDS/ICDD) provides standard x-ray powder patterns and develops new methods for quantitative x-ray diffraction analysis, XRD profile analysis, and powder characterization. Under this program, an eight-person group of Research Associates, supported by JCPDS/ICDD, works at NBS under the technical direction of a Division staff member, to provide this standard x-ray data.

Other cooperative programs with the private sector include a Research Associate program with Mobil Oil which has led to development of methods to identify and measure arsenic compounds in shale oil, critical to protecting process catalysts in this area of synthetic fuel technology. Cooperative programs with more than a dozen companies in the petroleum industry have established a basis for quality control assessments of lubricants and their oxidation stability. In the ceramic area, we have collaborated with various capacitor manufacturers such as Union Carbide to develop better fracture test methodology needed for improved mechanical reliability and with manufacturers such as Cummins Engines to evaluate the friction and wear properties of ceramics for advanced heat engine applications. In cooperation with Bell Laboratories and the Reactor Division, we have refined the structural chemistry characteristics of fast ion conductor materials, important to further development of high-energy batteries.

The Division also maintains strong contacts with the academic community. It is closely associated with the recently established industry-academic ceramic processing centers at MIT and Rutgers University and funds selected research programs such as a project at the University of Maryland in sol-gel process chemistry. Distinguished faculty members from MIT, Ohio State, Northwestern, and the University of Minnesota have spent varying periods of time working in the Division's laboratories during the past year.

Joint programs with other government agencies provide critically needed data and measurement methods. Our ceramic processing program provides, for example, fluorescence standards to the U.S. Postal Service, data on the chemical and mechanical properties of structural ceramics for the Department of Energy, and information on properties of microwave window materials to the Department of Defense. The Mechanical Properties Group assists the Department of Defense in developing proof-testing methodology for carbide and nitride ceramics in heat engine applications, and erosion and wear data to reduce machining costs and predict materials performance. Our Glass group provides tailored glasses for DOE applications in laser fusion research and data to support DOD needs for advanced fiber-optic materials. Our research supports a major development of new antifoulant coating technology by the Navy and provides the measurement methods needed to assess the environmental impact of this new development. The development and production of Standard Reference Materials (SRM) and Reference Materials (RM) is another major Division activity. Overall, the Division has responsibility for over 100 different SRMs and RMs. These cover a diverse variety and include standards for qualitative and quantitative x-ray diffraction analysis, property standards for control of processing in the glass industry, and compositional standards for

particulate and surface analysis. Currently, some 25 new SRMs are under development to meet new and demonstrated user needs in areas such as particle size measurements, glass property determinations, compositional analysis, and lubricant chemical characterization.

The technical program of the Division is divided into five major task areas. The research activities and recent technical accomplishments carried out under each task are described in detail in Section 3 of this report. Summarized below are brief descriptions of the Division research tasks.

(1) CERAMIC PROCESSING AND CHARACTERIZATION

Investigates chemical and physical processes important to producing reliable and durable ceramic materials. Emphasis is given to establishing the controlling parameters affecting microstructure and property evolution at all stages of the ceramic processing cycle from powders to fully densified bodies. Activities include advanced powder synthesis techniques, powder and compact characterization, and structural chemistry of ceramic materials. X-ray SRMs and standard powder patterns, developed in cooperation with JCPDS/ICDD, are produced in this task.

(2) HIGH TEMPERATURE MATERIALS CHEMISTRY FOR PROCESSING AND DURABILITY

Investigates the thermodynamic and kinetic behavior of materials in high-temperature/high-pressure process and service environments. Phase equilibria of ceramic and glass systems are determined through modeling and experiment. The Phase Diagrams for Ceramists Data Center, included in this task, compiles and evaluates ceramic phase diagrams in cooperation with the American Ceramic Society.

(3) MECHANICAL PROPERTIES OF CERAMICS

Investigates processes affecting the structural reliability and performance of ceramics and glass at ambient and high temperatures and in aggressive environments. Theoretical and experimental work is directed to understanding of fracture and deformation mechanisms and their relationships to microstructure.

(4) GLASS AND OPTICAL MATERIALS

Investigates processes involved in synthesis, forming, and uses of glasses and optical materials, including thin films. Activities include development of SRMs needed by the glass industry and others, such as those for viscosity, resistivity, dielectric constant, thermal expansion, and chemical composition; optical properties of glass; and process-structure-property relationships in thin films of glasses and ceramics.

(5) MATERIALS PROCESSING AND DURABILITY CHEMISTRY

Investigates chemically and biologically mediated processes affecting processing and durability of inorganic materials. Activities currently include research in microbial corrosion of metals, bioprocessing of metals, and combined chemical and mechanical factors in friction and wear, including the tribology of high-performance ceramics. The Division's work on recycled oil has also been carried out under this task.

2. PERSONNEL AND THEIR RESEARCH

Blackburn, Douglas H.	<ul style="list-style-type: none">● Special glass formulations● Glass processing● High modulus glass● Glass standards for microprobe analysis
Blair, William R.	<ul style="list-style-type: none">● Ultratrace metals speciation● Biotransformations of metals● Environmental durability of coatings● Element-special chromatography
Block, Stanley	<ul style="list-style-type: none">● Structure and polymorphism of materials● Ultra high pressure properties● Crystallography● Generation/measurement of high pressures
Bonnell, David W.	<ul style="list-style-type: none">● High temperature-pressure mass spectrometry● Computer modeling● Vapor transport
Brinckman, Frederick E.	<ul style="list-style-type: none">● Environmental metal transport● Materials durability (predictors)● Organometallic chemistry● Biological mediation of surface chemistry● Ultratrace metal speciation
Cellarosi, Mario J.	<ul style="list-style-type: none">● Glass SRM development● Glass recycling● Glass properties
Chuang, Tze-Jer	<ul style="list-style-type: none">● Ceramics● Diffusional crack growth● Finite element analysis● Creep theory
Chuck, Leon	<ul style="list-style-type: none">● High temperature mechanics● Scanning electron microscopy● Acoustic monitoring of cracks
Cook, Lawrence P.	<ul style="list-style-type: none">● Phase equilibria of ceramics (modeling & experiment)● Phase diagrams for ceramists (data center)● Electron microscopy● Thermodynamics
Coyle, Thomas D.	<ul style="list-style-type: none">● Inorganic and Organometallic Chemistry● Chemistry of Materials Processing and Durability

Dragoo, Alan L.	<ul style="list-style-type: none"> ● Transport properties of ceramics ● Corrosion of structural ceramics ● Ceramic powder synthesis ● Ionic conducting ceramics--electrical properties
Farabaugh, Edward N.	<ul style="list-style-type: none"> ● Thin film production and analysis ● X-ray diffraction analysis ● Scanning electron microscopy
Feldman, Albert	<ul style="list-style-type: none"> ● Optical properties ● Solid state physics ● Elasticity and photoelasticity ● Interferometry, ellipsometry, refractometry
Frederikse, Hans	<ul style="list-style-type: none"> ● Electrical and mass transport in solids ● Electrical conductivity at very high temperature ● Depth profiling (Rutherford backscattering)
Freiman, Stephen W.	<ul style="list-style-type: none"> ● Ceramics and glasses ● Fracture mechanics ● Mechanical properties, environmental effects
Fuller, Edwin R.	<ul style="list-style-type: none"> ● Atomistic models of fracture ● Fracture mechanics of ceramics ● Fracture, environment-assisted ● Mechanical properties at high temperature
Gates, Richard	<ul style="list-style-type: none"> ● Friction and wear of materials ● Wear mechanisms and analysis ● Engine condition monitoring ● Ferrography
Gonzalez, Armando	<ul style="list-style-type: none"> ● Mechanical reliability of ceramics ● Mechanical testing ● Microstructure analysis
Grabner, Ludwig H.	<ul style="list-style-type: none"> ● Optical properties ● Testing and Measurements ● Spectroscopy
Haller, Wolfgang K.	<ul style="list-style-type: none"> ● Glass properties, manufacture and use ● Structure of glass ● Sol-Gel processes ● Fine (small) particles
Hastie, John W.	<ul style="list-style-type: none"> ● High temperature processes--inorganic materials ● Phase equilibria, solution models ● High temperature-pressure mass spectrometry
Hockey, Bernard J.	<ul style="list-style-type: none"> ● Ceramics ● Deformation and wear ● Scanning and transmission electron microscopy

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| Hsu, Stephen M. | <ul style="list-style-type: none"> ● Tribology ● Oxidation mechanisms of organic mixtures ● Lubrication and wear mechanisms ● Molecular structural effects of frictions and wear |
| Hubbard, Camden R. | <ul style="list-style-type: none"> ● Computerized x-ray diffraction techniques ● Quantitative x-ray diffraction methods ● X-ray diffraction standard reference materials |
| Iverson, Warren P. | <ul style="list-style-type: none"> ● Biocorrosion of metals ● Microbial extraction/uptake of metals ● Ceramic and stone biodeterioration ● Fluorescence |
| Jewett, Kenneth L. | <ul style="list-style-type: none"> ● Organometallic speciation ● Trace element detection ● Analysis of organic mixtures ● SRM research |
| Krause, Ralph J. | <ul style="list-style-type: none"> ● Chemical equilibria ● Geothermal cements, mechanical properties ● High pressure-high temperature testing ● Vapor pressure measurements |
| Ku, Chia-Soon | <ul style="list-style-type: none"> ● Oxidation kinetics of complex organic mixtures ● Base oil compositional effects ● Modeling of reaction systems |
| Lawn, Brian R. | <ul style="list-style-type: none"> ● Structural reliability ● Fracture mechanics ● Contact phenomena ● Erosion and wear |
| Mauer, Floyd A. | <ul style="list-style-type: none"> ● X-ray diffraction instrumentation ● X-ray diffraction under controlled environments ● P, V, T data of inorganic materials |
| McDaniel, Clyde | <ul style="list-style-type: none"> ● Ceramics ● Creep ● X-ray diffraction |
| McHale, Anna E. | <ul style="list-style-type: none"> ● Electrical properties of ceramics ● Synthesis of dielectric ceramics ● Ceramic processing |
| Munro, Ronad G. | <ul style="list-style-type: none"> ● Theory and modeling ● Equations of state ● Molecular dynamics of phase stability ● Structure of amorphous materials |

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|-----------------------|--|
| Olson, Gregory J. | <ul style="list-style-type: none"> ●Metals biocorrosion ●Bioprocessing industrial materials ●Eqifluorescence microscopy imaging ●Surface modification and bioadhesion |
| Ondik, Helen M. | <ul style="list-style-type: none"> ●Phase diagrams for ceramists data center ●Materials properties for coal conversion use ●Data compilation systems |
| Parks, Edwin J. | <ul style="list-style-type: none"> ●Macromolecular organometallic chemistry ●Bioactive polymers ●Ultratrace metal speciation ●Controlled-release polymers |
| Pei, Patrick | <ul style="list-style-type: none"> ●Separation of complex organic mixtures ●Trace organic compound identification ●Differential scanning calorimetry |
| Perloff, Alvin | <ul style="list-style-type: none"> ●Analytical microscopy ●Processing of ceramic powders ●X-ray structural analysis |
| Piermarini, Gasper J. | <ul style="list-style-type: none"> ●Pressure/temperature effects on materials ●Generation and measurement of ultra high pressures ●Physical and structural properties of materials ●X-ray diffraction, phase relations, optical measurements |
| Plante, Ernest R. | <ul style="list-style-type: none"> ●Ceramics ●Knudsen effusion mass spectrometry ●Vaporization ●Thermodynamics |
| Rhyne, Kay V. | <ul style="list-style-type: none"> ●Ceramics ●Small angle neutron scattering ●Nondestructive analysis |
| Ritter, Joseph J. | <ul style="list-style-type: none"> ●Synthetic inorganic chemistry ●Ceramic powders from organometallic precursors ●Ceramic powders from gas phase, solution and gel reactions |
| Robbins, Carl R. | <ul style="list-style-type: none"> ●Fine ceramic particulate properties and characterization ●Spray drying; powder preparation ●Quantitative microscopy and x-ray diffraction |

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|------------------------|---|
| Roberts, Ellis C. | <ul style="list-style-type: none"> ● Mechanical testing ● Erosion and wear |
| Roth, Robert S. | <ul style="list-style-type: none"> ● Crystal chemistry of ceramic materials ● Phase equilibria ● Dielectric, semiconducting, and ionic conducting ceramics ● Phase diagrams for ceramists data center |
| Sanders, David M. | <ul style="list-style-type: none"> ● Thin film production, characterization, and properties ● Amorphous and crystalline inorganic films ● Glass vapor pressure ● Diffusion |
| Schenck, Peter K. | <ul style="list-style-type: none"> ● Laser spectroscopy ● Temperature measurement ● Computer graphics |
| Schneider, Samuel J. | <ul style="list-style-type: none"> ● Ceramic processing ● Structural ceramics and composites ● Phase equilibria ● High temperature measurements ● Ceramics for energy applications |
| Tighe, Nancy J. | <ul style="list-style-type: none"> ● Ceramics ● Creep at high temperatures ● Mechanical properties, high temperature ● Scanning and Transmission electron microscopy |
| Waring, Jon L. | <ul style="list-style-type: none"> ● Phase equilibria of ceramics ● High pressure effects ● Corrosion of structural ceramics |
| Weeks, Stephan | <ul style="list-style-type: none"> ● Atomic fluorescence--trace elements ● Chemiluminescence--organic mixtures ● Laser spectroscopy |
| White, Grady S. | <ul style="list-style-type: none"> ● Ceramics and glass ● Nondestructive evaluation ● Subcritical crack growth |
| Wiederhorn, Sheldon M. | <ul style="list-style-type: none"> ● Ceramics ● Erosion ● Fracture processes ● Mechanical properties at high temperatures and pressures |

3. RESEARCH ACTIVITIES

3.1 CERAMIC PROCESSING AND CHARACTERIZATION

Major task objectives concentrate on the development of theory, measurement methodology, standards, and data for producers and users of technical and bulk ceramics. Other materials also are researched when specialized data and measurements techniques necessary for this task require improvement for application to ceramic systems. Emphasis is on the scientific aspects of processing (powders through densification) and new concepts important to the development by industry of improved and more reliable ceramics.

Ceramic processing activities were expanded and consolidated during the year with major emphasis on new facilities, technical programs, and collaborative efforts. Six new laboratories: Powder Measurement and Characterization, Rutherford Backscattering (RBS), Quantitative X-ray Diffraction (XRD), Compaction and Densification, Laser Processing, and Chemical Precursor Processing are at various stages of completion. High pressure research was initiated on transformation toughened ceramics and on grain growth and sintering processes. Phase diagram work was integrated with new programs involving ceramic powder synthesis by unconventional methods and theoretical modeling of phase equilibria and structure/property calculations.

Significant collaborations with groups in and external to NBS were continued or established to strengthen all task programs. Mutual aid and expertise were provided through associations with the Joint Committee for Powder Diffraction Standards-International Centre for Diffraction Data (JCPDS-ICDD) and the Phase Diagrams for Ceramists (PDC) Data Center at NBS. Dr. R. Snyder, Alfred University, cooperated in quantitative XRD research. Dr. E. Case, University of California, helped establish an expanded program on characterization of ceramics by small angle neutron scattering (SANS). Dr. R. Coble, Massachusetts Institute of Technology, provided valuable overall consultation and collaborated in high pressure research. Dr. C. Semler, Ohio State University, helped initiate new research on toughened glass/ceramic materials. Drs. A. Cormack and R. Catlow, University College London, contributed computer simulation structure and lattice imaging calculation capability within the Division. In addition, two guest workers from private industry, three co-op students, two postdoctoral associates (an additional two ceramics scientists appointed for FY84), and several foreign scientists participated actively in task activities.

A major NDE program on green state ceramics was established with Argonne National Laboratory and a program on toughened ceramics is under discussion with scientists from Westinghouse Laboratories. Development of further collaborative efforts with Massachusetts Institute of Technology, Rutgers, Ohio State University (all on ceramic processing), International Business Machines (multilayer capacitors), and Bell Telephone Laboratories (dielectric ceramics) is in progress. Partial funding for research was provided by various divisions in the Department of Energy, Department of Defense, U.S. Postal Service, and several offices (OSRM and ONDE) at NBS. Major research activities are summarized by the following subtask areas:

1. Processing, properties, and characterization of ceramics;
2. Phase diagrams and structural chemistry, experimental and theoretical, of materials at elevated temperature and pressure; and
3. Evaluation and compilation of data.

Subtask 1 emphasis is on research involving the ceramic processing cycle (powder synthesis, compaction, densification) and relevant characterization and properties. It is linked to Subtask 2 but concentrates on non-conventional chemical routes and techniques for ceramic processing. A program on NDE and small-angle neutron scattering (SANS) characterization of green ceramic compacts was initiated in cooperation with the Mechanical Properties Group, and several new processing/characterization laboratories are near completion. Quantitative XRD techniques, standards, characterization data, and theory for powders, as well as for consolidated and densified products, also are an integral part of this subtask.

Phase equilibria and structural chemistry research on powdered and single crystal materials at elevated temperature and pressure, using a variety of techniques in Subtask 2, provide a basic framework of knowledge and permit testing of concepts necessary for Subtask 1. Experimental work is in progress on the thermochemistry and structure of several electronic ceramics and on pressure-induced transitions in toughened ceramics based on zirconia (ZrO_2). Theoretical research on modeling and prediction of structure/property relations and P,T structural mechanisms and chemistry was initiated to help guide future experimentation.

Subtask 3 describes collaborative efforts with the JCPDS Associateship at NBS.

FY83 Significant Accomplishments:

- o Implemented a variety of theoretical investigations to guide phase diagram and processing research within the task. They include:
 - modeling of complex oxide systems by cluster variation techniques;
 - structure/property calculations of materials by computer simulation methods;
 - calculation of high resolution lattice images based on the Cowley-Moody multi-slice technique;
 - calculation of phase diagrams, including pressure-induced transitions, by molecular dynamic computer simulation techniques.
- o Measured P,T phase relations in ZrO_2 -based materials to explore novel mechanisms to toughen these ceramics and determined phase equilibria in the ZrO_2 - TiO_2 (plus additives) systems relevant to subsequent processing of dielectric ceramics.

- o Ceramic multicomponent powders and densified coatings, stable and metastable, were synthesized by the development of a variety of novel techniques based on chemical precursors (ZrTiO_4 , $\text{Ca}_2\text{SiO}_4/\text{MgO}$, and $\text{CeO}_2/\text{Y}_2\text{O}_3$) and on heterogeneous solid/gas reactions ($\text{SiC}/\text{Si}_3\text{N}_4$) by localized laser heating. Demonstrated that the method of ceramic processing used in producing $\text{CeO}_2/\text{Y}_2\text{O}_3$ materials strongly influences their electrical properties.
- o Processed and measured ceramic compacts containing controlled defects by SANS and demonstrated that neutron scattering is by a multiple refraction mechanism, the magnitude of which changes from the unfired state through binder burnout and initial sintering. Established cooperative NDE program on unfired ceramics with ANL.
- o Measured grain growth and sintering of model ceramic powders (LiF , NaCl , and MgO) at elevated pressure to determine the influence of this variable on sintering models and theory.
- o Developed improved standards, techniques, and computer programs for quantitative phase analysis of ceramic materials by XRD. Established a Quantitative XRD Laboratory and completion of five new ceramic processing and characterization laboratories is in progress.
- o Developed methodology and measured the electrical characteristics of boron nitride materials for microwave applications up to 2300°C . Demonstrated how these materials could be improved when processed in composite form. Obtained experimental evidence that SO_2 , even in the ppm range, promotes nitridation of SiC -based structural ceramics at elevated temperature by several possible mechanisms. The result may be detrimental for densified SiC materials but the basic chemistry may be applicable to nitridation of powders and compacts. Developed processing methods and materials for luminescent standards required by the U.S. Postal Service to process all mail.

Ceramic Processing, Properties, and Characterization

Subtask 1

T. Negas, S. Block, J. Dillon, L. P. Domingues¹, A. L. Dragoo, H. P. R. Frederikse, C. Hubbard, A. E. McHale, R. G. Munro, A. Perloff, G. J. Piermarini, J. Ritter, C. Robbins, R. S. Roth, C. Semler², J. Simmins, J. L. Waring

¹Guest Worker, Trans-Tech, Inc.

²Guest Worker, Ohio State University

During the year, substantial progress was made in developing improved facilities necessary for task research. An expanded, centralized laboratory was completed for continued work in quantitative x-ray analysis of powders, compacts, and finished microstructures. Computer equipment for this laboratory and for activities of the JCPDS were consolidated within a separate data processing complex. New video

recording capability was incorporated into the existing diamond anvil pressure cell (DAPC) facility to permit quantitative characterization of phase transitions by birefringence variations.

A major new laser processing and synthesis facility, complete with diagnostics and sampling capability by mass spectrometry, is under construction. RF and microwave equipment also are included to conduct comparative processing experiments or to couple with the laser processing as necessary.

Four additional facilities are at various stages of completion. A Rutherford Backscattering (RBS) laboratory was planned in cooperation with A. O. Wasson of the Center for Radiation Physics. RBS uses MeV-ions from a Van de Graff accelerator (protons, α -particles) for nondestructive, composition analysis of materials by depth profiling (up to 2 μm). The technique can be applied to nearly any type of material for a wide variety of problems associated with diffusion, corrosion, surface hardening, thin films and coatings, and particulate systems. An RBS chamber was designed and ordered, and additional equipment is in the procurement or assembly stage.

Compaction/Densification and Chemical Precursor Processing Laboratories are under construction. The former includes equipment for conventional hard-die and isostatic pressing, sedimentation, hot-pressing, and pressureless sintering. As funding becomes available, a dilatometer will be incorporated with the hot-press to monitor shrinkage. A HIP furnace also was purchased specifically for ceramics but will be part of a control unit located in Metals Processing. The Precursor Lab will be devoted to low temperature chemical routes and techniques such as sol-gel and homogeneous coprecipitation to synthesize reactive submicron particulates. Particle conditioning research using electrophoresis techniques also will be conducted.

Although much of this task deals with powders at some stage of research, it has lacked the means to measure, characterize, and manipulate the particulates produced using dedicated facilities. Thus, a Particle Measurement and Characterization Laboratory was established. This laboratory includes state-of-the-art measurement capabilities related to particle size and distribution, agglomeration, density, and surface area. Also, equipment is available to mill, fraction, characterize, and generate submicron particulates normally required for enhanced sinterability. The laboratory will characterize and prepare for compaction, powders synthesized from precursors and will collaborate with Metals Processing according to their needs. In addition, it will provide physical property measurements and data on powders that can be cross-correlated with XRD (see below), microscopy, and image analysis measurements. This laboratory also will provide the necessary property measurements that help link processing with microstructural evolution in future task programs.

Powder Synthesis

ZrTiO_4 is an attractive ceramic for microwave resonator applications. It has a relatively high dielectric constant (35 to 40) and a TC_k

tuneable with substitutions of SnO_2 ($\text{Zr}_x\text{Sn}_y\text{Ti}_z\text{O}_4$, $x+y+z = 2.0$).

Conventional calcined powders require 1550 to 1650 °C to densify via pressureless sintering, and doped ceramics are difficult to process due to vaporization of SnO_2 . Thus, commercial ceramics are densified by liquid phase sintering (1350 to 1400 °C) using additives, such as rare-earth and transition metal oxides. Microstructures lack uniformity and the associated grain growth enhances "pullouts" during machining. Sintering aids also increase the dielectric loss (decrease quality factor, Q) to less than optimal levels (Processing and Properties of ZrTiO_4 -Based Ceramics, McHale, Negas, Ritter, Roth, and Domingues, Zirconia-83, Stuttgart, June 1983). Phase equilibria and structural research (see Subtask 2) revealed additional problems that could be resolved using nonconventional powder synthesis techniques.

Two variations of a low temperature, modified sol-gel technique based on alkoxide precursors were developed to prepare homogeneous ZrTiO_4 -based powders. Basically, titanium iso-propoxide is dissolved either in toluene or in isopropyl alcohol. Zirconium-n-butoxide or zirconium tetra-acetate is added to the solution. After slow hydrolysis to establish hydroxyl linkages among Zr-Ti organic complexes and, finally, liberation of alcohol groups, precipitation occurs at pH = 8.0 to produce a gel amorphous to x-rays. After drying the gel at 100 to 120 °C and calcining in the 450 to 600 °C range, ZrTiO_4 crystallizes metastably at temperatures ~ 600 °C lower than in conventional methods. ZrTiO_4 decomposes below ~ 1125 °C (Subtask 2) which means that blended ZrO_2 and TiO_2 powders react only above this temperature. ZrTiO_4 powders also were produced from TiCl_4 plus ZrCl_4 in 12 N HCl. As tin tetrachloride also can be stabilized in this medium, the technique permits synthesis of $\text{ZrO}_2 \cdot \text{TiO}_2 \cdot \text{SnO}_2$ precursors when precipitated with ammonium hydroxide. Reaction details have not been investigated completely, especially with respect to formation of metal oxychloride which would be a detrimental impurity. Future studies will include methods to dry, de-hydroxylate, compact, and densify these submicron powders.

Hydrolysis and precipitation of homogeneous zirconium titanate solid solutions with Zr/Ti contents between 17/3 and 1/4 also were shown to be possible using metal-alkoxide precursors. Crystallization of precursors at 650 °C yields single phase, metastable products at every composition; the structure being disordered, orthorhombic ZrTiO_4 near Zr/Ti = 1.0 or tetragonal near compositional extremes (tetragonal zirconia or rutile). Equilibration of these coprecipitated powders was used to help determine phase relations in the system at $T < 1200$ °C (see Subtask 2). The metastable tetragonal zirconia solid solution powders coarsen during anneals at temperatures above 1000 °C and transform martensitically to the monoclinic variant on cooling. This suggests that these materials could be used to process alternative transformation toughened ceramics that normally contain particulates of $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ or $\text{ZrO}_2(\text{MgO})$ solid solution.

Transformation toughening (TT) of densified ceramics has attracted considerable international interest and research effort. Emphasis, however, has been limited entirely to toughening associated with the martensitic, tetragonal \longleftrightarrow monoclinic transition of ZrO_2 , including

solid solutions with Y_2O_3 of MgO. Subtask 2 identifies a promising alternative concept. Processing of (TT) ceramics, relies on methods to obtain fine particles of a metastable structure and on the ability to retain or obtain this variant without substantial grain growth and spontaneous transformation after densification at elevated temperature. Chemical precursor techniques to synthesize the metastable powders at low temperature appear to be most attractive. Alternatively, controlled homogeneous or heterogeneous nucleation of the desired material from a monolithic glass or powdered glass is a possible approach.

A review of the mineralogical and cement literature has identified two crystalline silicates that undergo martensitic transitions. These include the proto-, ortho-, and clino-enstatite transitions for $MgSiO_3$ and, at least, one transition for Ca_2SiO_4 . $MgSiO_3$ is chemically compatible with Mg_2SiO_4 and cordierite ($Mg_2Al_4Si_5O_{18}$, ideally), two commercial dielectric substrate materials. The latter is under investigation by International Business Machines for alternative, low thermal expansion, multilayer capacitors. Ca_2SiO_4 is chemically compatible with MgO used in conventional refractories and castables. Martensite transitions for both silicates could be harnessed to toughen these ceramic matrices, and the general phenomenon could be researched using new materials apart from ZrO_2 .

Preliminary experiments were performed using homogeneous glass (D. Cronin, Glass Group) having a bulk composition on the $MgSiO_3$ -cordierite join. Cordierite plus metastable ortho- or proto- $MgSiO_3$ were nucleated homogeneously at 1300 °C to obtain a polycrystalline ceramic after cooling to room temperature. When polished, the ceramic surface transforms to clino- $MgSiO_3$ and microfissures, suggesting that the transformation can be induced by stress. Further experiments are in progress to measure (by XRD) and control critical crystallite size for transformation, optimum bulk composition, and ultimate mechanical properties. Transformations for pure $MgSiO_3$ are under investigation using reactive powder prepared from alkoxides and acetates (see below).

Experiments with Ca_2SiO_4 -MgO ceramics have concentrated on low temperature powder processing using alkoxides and acetates because glasses are difficult to prepare from the oxides (e.g., the eutectic for the system is > 1800 °C). Ca_2SiO_4 was synthesized from silicon alkoxide plus calcium acetate with addition of ammoniacal ammonium oxalate. MgO plus Ca_2SiO_4 powders also were prepared using similar methodology. Quantitative yields of coprecipitated products were obtained recently and studies on their crystallization behavior versus temperature are in progress.

Laser Processing

Research concentrates on laser induced heterogeneous chemical reactions localized at a solid-gas interface. Potential applications include ceramic coatings with controlled microstructures on substrates and reactive sintering of porous compacts of precursor powders. Future efforts also will be directed to the synthesis of ultra-fine reactive oxide powders from solid and gaseous metal chlorides with oxygen. Exploratory experiments were performed using powders of Si plus C, Si,

and Mo, preshaped by hard-die pressing, and reactive gases such as $(\text{CN})_2$ and CH_4 . Composite $\text{SiC}/\text{Si}_3\text{N}_4$, SiC , and molybdenum carbide coatings were synthesized without disturbing the geometry of the original compacts. Activities will expand as the laser facility becomes fully operational.

Green State Ceramics

Proven reproducibility and reliability of ceramic components are needs that can be accomplished only by a combination of processing controls and NDE procedures together with a fundamental understanding of how defects arise and evolve within the processing cycle. This program focuses on the early stages of ceramic processing, the "green state," which consists of an assemblage of particulates loosely consolidated by forming methods and often containing binders, moisture, and other additives that normally are "burned out" during a preliminary calcination step. The green part, therefore, constitutes a reservoir of accumulated processing flaws and imperfections (voids, pressure or particle packing heterogeneities, fissures, agglomerates, inclusions, etc.) that persist and/or generate new defects during subsequent processing. Ideally, characterization and rejection of parts should begin at this stage, but virtually no work has been done on the properties of green compacts. Reliable methods to detect and relate initial flaws to final structural imperfections, therefore, have not been demonstrated.

Research consists of the following related elements:

- (a) processing of generic green ceramics containing flaws of controlled size and distribution;
- (b) characterization of these compacts through final microstructural evolution, primarily by microscopy and small angle neutron scattering (SANS); and
- (c) evaluation of potential NDE methods cross-correlated with characterization measurements.

During this year, a cooperative program was established among NBS, Argonne National Laboratory (ANL), and a guest worker, Dr. Eldon Case, Univ. of Calif., Berkeley. NBS is responsible for all aspects of green state processing and pertinent characterization measurements. ANL is conducting exploratory NDE measurements based on ultrasonics, microfocus radiography, and NMR on the green compacts and on those also subjected to binder burnout and final densification.

Two classes of green ceramics are under investigation. YCrO_3 -based compacts, when fully densified, provided the first model ceramic materials used to apply diffractive mode, SANS techniques and theory (see Annual Report, 1982) to the detection and characterization of finely distributed defects (microfissures) in the 2 to 200 nm size range. Green compacts of these materials were characterized by NDE (at ANL) and by SANS (at NBS) methods. Promising preliminary results were obtained (see below) and emphasis was turned to a broad range of generic green state defects that encompass agglomerates, impurity inclusions, and

heterogeneous packing of particles. These features can all be simulated in one type of green composite ceramic consisting of a relatively uniform matrix of fine particles containing a distribution of densified, large spheres. MgAl_2O_4 (spinel) was selected for both the matrix and "hard" spheres to maintain constant chemistry and minimize thermal expansion and conductivity mismatch for subsequent processing and characterization. Three sets (ten specimens each) of these materials having 0, 2, and 20 percent volume fractions of agglomerates in the 75 to 100 μm range were fabricated for investigation. In addition, specimens from each set were calcined at 700 °C to remove organic binders and then sintered at 1500 to 1550 °C to obtain final densification. Measurements on these latter materials permit monitoring of the evolution of flaws from the green state to the finished microstructure. Figure 1A illustrates a typical green composite as processed. After densification, figure 1B, new flaws (pores) have developed, adjacent to the spherical agglomerates, indicating that the matrix phase detaches due to faster densification (greater shrinkage). The detrimental effect of these defects also is reflected by final bulk density. Without agglomerates, green compacts densify to near 98 percent of theoretical, while the materials loaded with 2 and 20 percent attain approximately 94 and 85 percent, respectively.

Characterization by SANS and NDE

Small angle neutron scattering from materials is characterized by two dominant regimes, diffractive (DS) and multiple refractive scattering (MRS). The DS mode yields microstructural information for the 2 to 200 nm size range. However, the MRS mode is potentially more useful for the green state as larger, micron-size defects can be detected. In cooperation with Dr. E. Case, Reactor Division staff, and the Mechanical Properties Group (E. Fuller and K. Hardman-Rhyne) numerous exploratory measurements were made on YCrO_3 and MgAl_2O_4 green compacts. Using six neutron wavelengths (4.85, 5.45, 6.25, 7.0, 8.0, and 9.0 Å), it was demonstrated that MRS is the dominant mechanism. The specimens show typical beam broadening (full width at half maximum FWHM) with a linear dependence on λ^2 and a circularly symmetric Gaussian profile (see also Mechanical Properties, Porosity in YCrO_3 by SANS). The data demonstrate remarkable reproducibility and the ability to detect small changes in scattering intensity from different samples. Processing history and microstructure evolution also can be followed by changes in MRS as demonstrated by a progressive increase of scattering centers for a MgAl_2O_4 green compact (no agglomerates, plus binder) after calcination at 700 °C and at 975 °C.

To date, SANS experiments using green compacts are yielding preliminary information that demonstrates differences among materials. Future research will be devoted to a critical analysis of these data combined with an evaluation of existing and new models and theory for MRS, especially linked to the specific type of scattering centers (defects) in green ceramics. This work also is applicable to the characterization of heterogeneities in compacts produced by slip-casting, sedimentation, and gelation methods. A high temperature furnace for SANS also was constructed to continuously monitor microstructural flaws in situ throughout the processing cycle.

In collaboration with Dr. D. S. Kupperman, ANL, ultrasonic studies of YCrO_3 and MgAl_2O_4 -based green ceramics are in progress. Two YCrO_3 specimens were examined with both longitudinal and shear waves. Surprisingly, no liquid couplant was necessary to propagate these waves, and the shear-wave velocity varied with polarization, indicating elastic anisotropy. The latter observation may be due to the fact that the compacts were first hard-die, uniaxially pressed before isostatic compaction. This result could be most significant if it can be established that density gradients from the former processing step are carried into and "imprinted" within the latter.

Preliminary ultrasonics measurements on MgAl_2O_4 green compacts show that the frequency spectrum for these materials is within 0 to 2.0 MHz and that the spectra, as in SANS, are different for each material measured, suggesting anomalous microstructure. Additional research is necessary to determine sensitivity of ultrasonics using green compacts containing smaller flaw sizes and populations, as well as sintered materials.

Densification, Microstructure, and Properties

Ceria-Based Ceramics

High-density, yttria, and gadolinia-doped ceria ceramics were found to exhibit notable differences in electrical properties which correlated with differences in the processing methods used to form the materials. Samples with dopant concentrations of 8.5 and 30 mol.%, with respect to cation concentration, were studied. Powder precursors for the formation of ceramic samples were prepared via (1) coprecipitation of carbonates from homogeneous solution; (2) decomposition of tartrate-ethylene glycol resins containing dissolved hydroxides; and (3) coprecipitation of hydroxides from homogeneous solutions. Most samples were thermally sintered. One sample with 8.5 mol.% Y was hot-pressed. Densities of samples ranged from 92 to > 99.5 percent of theoretical. The ac impedance of grain interiors (lattice impedance) and of grain boundaries and other inhomogeneities (inhomogeneity impedance) were measured over a frequency range of 50 Hz to 13 MHz, from 200 to 550 °C, in air. Lattice impedance appeared to depend primarily on dopant concentration, with the exception of the hot-pressed material for which a deviation from the general behavior was noted. Inhomogeneity impedance appeared to be influenced by calcination temperature, densification method, and dopant concentration. Microstructure examination and elemental analysis of samples by SEM/EDX showed Al to be an important contaminant both of grains and grain boundaries in the hot-pressed material. Although Al may be the source of different lattice impedance for the hot-pressed material, it is suggested that the lower sintering temperature and shorter sintering time used in hot-pressing results in a larger concentration of "deep traps" for oxygen vacancies in the ceramic. High Si concentrations were found to be associated with regions of large pores in gadolinia-doped materials.

Pressure Effects on Grain Growth and Sintering of Ceramics

In collaboration with Prof. R. L. Coble, of the Massachusetts Institute of Technology, a program on the effect of pressure on the grain growth and sintering of ceramic materials was initiated. NaCl was initially chosen as a model system to determine whether any effect was measureable. The experiments consist of two parts. First, a powdered sample is placed in a diamond anvil pressure cell (DAPC) to determine when the sample becomes pore free. Initially, the sample is opaque due to light scattering. When the sample becomes transparent, it is assumed to be nearly pore free. The second part involves heating the sample while varying time and temperature to determine when grain growth occurs. This is indicated by a change in Debye rings from a continuous to a spotty pattern. The NaCl becomes pore free at 2.56 GPa. At this pressure, the sample was heated for 10 minutes at 200 °C, and minimal grain growth was initiated. After heating at 300 °C for 16 minutes at pressure, grain growth was extensive, as indicated by a very spotty x-ray pattern. These results were encouraging, but because NaCl is very hygroscopic, LiF and MgO were investigated as potential model materials.

LiF becomes pore free at 2.96 GPa. Grain growth was not evident even after heating at 450 °C for two and one-half hours at pressure. However, when the pressure was lowered to less than 1.0 GPa, extensive grain growth resulted. It is thought that the grain growth is dependent on the diffusion rate and that the diffusion rate is related to the shape of the melting curve; i.e., if the melting point increases with pressure, then the diffusion rate will decrease. This concept will be explored in future experiments.

MgO behaves differently than NaCl or LiF in the manner by which it becomes transparent. In the range between 1.3 and 6.8 GPa, the sample becomes increasingly transparent. At 6.8 GPa and above, the MgO is pore free. ZrO₂, which is harder than any of the above materials, is not transparent at 16.1 GPa, the highest pressure currently attained in the x-ray studies.

Boron Nitride

Hexagonal Boron Nitride is a promising candidate for use as a microwave window material in space re-entry vehicles. As the material attains temperatures near 3000 °C for short durations, it is important to know the thermophysical/chemical properties of the ceramic. This work, supported by DOD, is concerned with the electrical conductivity, the dielectric behavior, and the vaporization chemistry of the material.

The dc electrical conductivity, σ , was measured (H. P. R. Frederikse and A. L. Dragoo) in a resistance-heated furnace equipped with tungsten heat shields. To avoid large electrical leakages at high temperatures that by-pass the sample resistance, two different experimental arrangements were devised: one uses a geometrical design in which the sample is isolated from the nitrogen gas in the main volume of the furnace, while the other achieves electrical isolation by means of a guard-ring configuration and an operational amplifier nulling circuit. Measurements were performed on several BN samples and BN/SiO₂ composites

up to about 2300 °C. The composites, provided by Dr. W. T. Messick of NSWC, appeared to have resistivities which exceeded that of monolithic BN by half an order of magnitude. The slope of the electrical resistivity vs reciprocal temperature corresponds to an activation energy of ~ 6.0 eV, in good agreement with optical studies of the intrinsic energy gap.

The investigation of the dielectric behavior (A. H. Kahn, Div. 562) involves calculation of the reflectivity (R), absorption (α), and transmissivity (Tr), of BN samples which have a high-conductivity surface layer and a nearly insulating main body, due to a surface temperature, T_s around 2500 to 3000 °C, and a steep temperature gradient, $\frac{dT}{dx}$, into the bulk. Computer calculations of R , α , and Tr were performed using various values of T_s , $\frac{dT}{dx}$, and σ . For surface layer conductivities of 1.0 to 0.1 ohm⁻¹ cm⁻¹, the reflectivity appears to be more than 98 percent. Within the main volume of the sample, the transmissivity shows an interesting oscillatory behavior as a function of thickness, caused by multiple reflection of the beam at the sample surfaces.

An analysis of several non-isotropic composite structures indicated that the transmissivity could be improved by using an alternating system of BN and SiO₂ lamina oriented with the lamina perpendicular to the outer surface of the window. When heated on the outer surface, the edges of the conducting BN layers would function like an optical wire-grid polarizer, allowing easy transmission for one polarization of microwave radiation.

Vaporization behavior of BN is under study by the High Temperature Processes Group.

Silicon Carbide

At relatively high oxygen partial pressures, such as in air, silicon carbide is protected from chemical attack by the formation of an impervious surface coating of silicon dioxide. However, at lower oxygen partial pressures, which may occur in some industrial processes and fuel-rich combustion conditions, SiC coatings and structural members may be subjected to continuous chemical attack. A study of reaction of silicon carbide ceramics with nitrogen, containing about 1000 ppm of SO₂, indicated that SO₂ promotes the nitridation of the silicon carbide by the formation of volatile carbon-sulfur compounds; principally CS₂ and COS. Silicon nitride and silicon oxynitride were found as solid reaction products on the silicon carbide. The reaction product layer was found to be porous and easily abraded. Results further suggest that gaseous sulfur species could contribute to favorable nitridation kinetics of Si compacts.

Ceramic/Glass Emission Standards

The USPS is designing and building a second generation phosphormeter that is used to measure luminescent intensity from materials such as stamps and for calibrating all mail sorting devices. This

instrumentation requires emission calibration standards that are mechanically durable and stable under prolonged exposure to UV or visible radiation. In cooperation with D. Cronin (Glass Group), processing techniques and materials having stable, reproducible emission properties were developed. These include the following:

- (a) densified $\text{Y}_5\text{Fe}_3\text{O}_{12}$ ceramic, no emission standard;
- (b) monolithic soda-lime glass, activated with Eu^{3+} , red fluorescent and red phosphor standards; and
- (c) densified glass activated with crystalline $\text{Zn}_2\text{SiO}_4\text{:Mn}$, green phosphor standard.

The USPS is now negotiating with private firms to obtain large quantity production based on NBS materials, properties, and processing specifications.

Quantitative X-ray Diffraction (QXRD)

Quantitative analysis requirements and applications are growing rapidly, particularly in the ceramics field. Two Standard Reference Materials (SRM) for quantitative analysis were completed this year--SRM 674 and a respirable quartz SRM (see below). To complement these SRMs, the set of programs, NBS*QUANT82 (see Annual Report 1982; C. R. Hubbard and R. L. Snyder, Alfred University) was distributed to over ten laboratories. Recent results comparing the use of a synthetic fly ash mixture, using (a) resolved lines only and (b) resolved and overlapped lines, clearly show the superiority of the latter method. This package of programs has been expanded with two new routines: ADDREGION and AMORPHOUS. Both are based on the same AUTO data file structure and are written in FORTRAN77 to simplify portability.

The program ADDREGION simply adds repetitive data sets for a given 2θ region. This is useful when low peak-to-background ratios are expected, such as in the nucleation of crystallites in glasses. A recent application involved measurement of a glass that was claimed to contain Pb crystallites. Nine repetitive data sets were collected and the summed data reveal no diffraction peak for Pb or for lead silicates. For comparison, a glass containing 0.1 percent Pt was scanned about five times faster, and the net peak intensity was 200 counts with an e.s.d. of about ten. Thus, the detection limit for Pt crystallites in this glass is about 0.01 percent, given a data collection time of 10 to 20 hours.

The program AMORPHOUS implements a modified spiking method which yields a direct measure of the weight fraction of an amorphous phase in a highly crystalline matrix. The two limitations to the method are finding a 2θ region on the amorphous halo free from Bragg reflection and choice of a background reference material. This method is being thoroughly evaluated in the course of certification of a respirable quartz SRM. The technique appears to be sensitive to small quantities (~ 5.0 wt.%) of an amorphous phase and, therefore, will prove valuable in the analysis of glass/ceramic composites, dielectric substrates such as cordierite, silicate-containing refractories, and structural ceramics such as SiC and Si_3N_4 .

XRD Intensity Standard Reference Materials 674 contains a set of five separate oxide powders. Each powder is certified for relative intensities of the major lines out to $2\theta = 70^\circ$ ($\lambda_{\text{CuK}\alpha} = 1.540598 \text{ \AA}$) and for the Reference Intensity Ratio (RIR). The average uncertainty in relative intensities and RIR value is about two percent. This set of SRMs is to be used for instrument intensity response calibration and for quantitative analysis by the internal standard, RIR method.

A Respirable Quartz SRM is nearly complete. The homogeneity of the 500 10 gm bottles was tested by several methods--particle size distribution, lattice parameter refinement, relative intensity, and RIR determination. All four analyses show the material to be homogeneous. Work is currently underway to certify the weight percent of crystalline $\alpha\text{-SiO}_2$ present. As no elemental or crystalline impurities were detected, the only possible second phase is amorphous SiO_2 . The modified spiking method was developed for this analysis by C. R. Hubbard, based on somewhat similar XRD measurements for polymers. Results from the method will be considered valid when three separate amorphous halo regions yield equivalent results. The choice of background reference material seems to be important for this requirement. A "zero background," off-cut, single crystal quartz plate appears to introduce a systematic variation in the weight percent (amorphous) with 2θ . A large grain size crystalline quartz is somewhat better but does not entirely remove the systematic variation. Spiking method results will be compared to results based on theoretical and experimental RIR constants and to analysis of powders washed in hot phosphoric acid which preferentially dissolves the amorphous SiO_2 . Complementary work on a cristobalite (SiO_2) SRM also was initiated.

A submicron crystallite size SRM is under development to calibrate quantitative measurements of particle size, strain, and compositional variation using the x-ray line-broadening (XLB) technique. A baseline material, MgO , with controlled cubic morphology was synthesized by the "smoke" method (Annual Report, 1982). Attention has turned to large batch SRM production using basic magnesium carbonate as a precursor. MgO powders with average grain sizes in the 100 to 300 \AA range were prepared from the carbonate calcined at 600 to 1350 $^\circ\text{C}$, 4 to 36 h, in air and nitrogen. Based on the results, four batches of MgO powder ($\sim 130 \text{ g}$ each) were prepared for XLB, microscopic, and image analyses necessary for future certification of the SRM.

Phase Diagrams, Structural Chemistry, and Theory

Subtask 2

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Theoretical Studies

Phase Diagrams via Molecular Dynamics

As part of a program to investigate phase diagrams at high pressure and temperature, a computer simulation technique is being utilized. In

particular, the new formulation of molecular dynamics, developed by Parrinello and Rahman at Argonne National Laboratory, is being used. This formulation is specifically intended for the study of structural phase transitions and is, therefore, applicable to the more general study of phase diagrams.

The first investigation of a phase diagram using this methodology was completed (Munro and Mountain, Phys. Rev. B, 1983). In this work, the phase diagram of lithium in the region $295 \leq T \leq 600$ K and $0 \leq P \leq 12$ GPa was studied. Excellent agreement between theory and experiment was obtained for (1) the room temperature bcc-fcc structural phase transition, (2) the temperature dependence of the bcc-fcc phase boundary, (3) the room temperature compression curve for the bcc and fcc phases, and (4) the bcc-liquid melting curve. Future efforts will concentrate on the calculation of phase diagrams (P-T-X) for zirconia-based ceramics.

Noncentral Forces in Ionic Compounds

Empirically, it is found for ionic compounds with cubic crystalline symmetry that the elastic constants C_{44} and C_{12} are not equal. This inequality is taken as evidence for noncentral forces (NCF). A force constant which combines the effects of several possible NCF interactions can be defined as,

$$f_o B = a_o (C_{44} - C_{12}) ,$$

where a_o is the nearest neighbor (NN) equilibrium bond length and $f_o = e^2/a_o^4$. Assuming that the NCF interactions involve primarily anions, values of B were plotted versus a_o for oxides and the respective halides. These results are shown in figure 2. For the chlorides, bromides, and iodides, the values of $f_o B$ are small, and the trends of these values are very similar; $f_o B$ decreases more rapidly for the fluorides and most rapidly for the oxides. These trends suggest that, for the oxides, the short-range repulsive interactions contribute significantly to $f_o B$; whereas, for the chlorides, bromides, and iodides, Van der Waals-type interactions make the major contributions to $f_o B$.

The oxide data can be approximated very well (correlation coefficient, -0.98) by an expression,

$$B = B_o \exp [-r_{NNN}/\rho] ,$$

where r_{NNN} , the anion-anion distance, $= a_o \sqrt{2}$. For the oxide data,

$$B_o = 12920 \text{ J/m}^2$$

$$\rho = 0.0434 \text{ nm.}$$

This value of ρ compares favorably with values computed quantum mechanically by Mackrodt and Stewart [quoted by J. H. Harding (J. Phys. Chem. 12:(19), 3931, 1979)] for oxygen-oxygen interactions in the alkaline earth oxides. Results from this work are applicable as input to other theoretical modeling and calculations in this Subtask.

Cluster Variation Models (CVM) and Theory for Phase Diagrams

CVM forms a hierarchical set of approximations for the configurational entropy of a system where the associated free energy is a function of energies and probabilities of occurrence of some small basic cluster of atoms. The methodology permits manipulation of these atomic clusters to minimize free energy functions which reflect stability or metastability of a phase in a computed phase diagram. Results are compared to experimental data and refined as necessary by further approximations. Thus far, CVM has been applied to simple metal alloy systems. Ceramic oxide systems are far more complex as larger clusters of many different atoms require consideration and calculation.

The CVM technique was used to predict phase relations in the $\text{CaCO}_3\text{-MgCO}_3$ and $\text{Fe}_2\text{O}_3\text{-FeTiO}_3$ systems. Both systems share a characteristic phase topology in which a line of second-order phase transition intersects a two-phase field at a tricritical point. Both $(\text{Ca, Mg})\text{CO}_3$ and FeTiO_3 order into trigonal (space group $R\bar{3}$) layer structures in which alternate basal planes $[(0001), \text{hexagonal}]$ are occupied by Ca and Mg or Fe and Ti. The ordering may be interpreted as a geometrical "escape" from the destabilizing effect of Ca-Mg or Fe-Ti (A-B) pair configurations in one crystallographic direction that simultaneously takes advantage of the stabilizing effect of (A-B) pair formation in another direction.

Although modeling of subsolidus order-disorder and phase separation phenomena now appear possible, CVM calculations also can be applied to liquid-liquid and solid-liquid phase relations. The power of the technique, as developed for model systems, is in the prediction of accurate phase diagrams and structures where sluggish reaction kinetics (e.g., at low temperature) preclude direct experimental verification. Systems of current interest include $\text{CaMgSi}_2\text{O}_6\text{-NaAlSi}_2\text{O}_6$ (multiple cation order-disorder) and MgAl_2O_4 (T-X dependent order-disorder).

Computer Simulation of Crystal Structures and Properties

A new cooperative program was initiated between Drs. C. R. A. Catlow and A. N. C. Cormack (University College London) and R. S. Roth, T. Negas, and B. Burton of NBS to apply computer simulation methods (CSM) to ceramic materials. The technique involves calculations of minimum potential energy functions to yield optimum bond lengths and angles for any given composition. Elastic and dielectric properties can be computed from the structural results. Multiphase interfaces and properties in ceramic systems, including important structural flaws such as point and planar defects, can be modeled, compared with experimental data, and ultimately predicted. The technique is under extensive evaluation using known structures and properties for dielectric materials in the BaO-TiO_2 system. Simultaneously, it is being applied to known low TC_k , high dielectric constant ceramics, $\text{BaNd}_2\text{Ti}_5\text{O}_{14}$ and $\text{Nd}_2\text{Ti}_9\text{O}_{24}$. Relevant structure-property experimental data are under investigation through collaborations with Dr. M. Zocchi (University of Milano), Dr. D. Kolar (University of Ljubljana, Yugoslavia), Dr. F. Glasser (University of Aberdeen, Scotland), Dr. A. Olsen (Arizona State University), and Dr. H. O'Bryan (Bell Telephone Laboratories). To

further implement this work, a computer program that calculates high resolution lattice images by the Cowley-Moody multi-slice technique was installed at NBS. Experimental lattice images obtained from the Division STEM facility can now be correlated with computed structures derived from CSM calculations to characterize property limiting defects in the angstrom range.

High Pressure Instrumentation

In the Annual Report for 1982, a novel type of microdiffractometer was described for use with synchrotron radiation in obtaining improved powder diffraction patterns from samples in the diamond anvil pressure cell (DAPC). The new instrument retains the fixed-angle feature of the energy dispersive method, that makes it adaptable for use with environmental chambers. Improved performance results from use of a channel-cut silicon monochromator to scan the wavelength of the incident beam. Since energy resolution of the monochromator is at least an order of magnitude better than that of solid state detector systems commonly used, a substantial improvement in resolution can be expected. At the same time, by using a detector with an annular slit to intercept the complete cone of radiation diffracted at a fixed angle of $2\theta = 12^\circ$, it is possible to increase the efficiency by a factor of twenty and to reduce the graininess that is typical of patterns from microscopic specimens.

Last year the feasibility of the method was demonstrated. Subsequent tests of a new instrument were conducted at the Cornell High Energy Synchrotron Source, CHESS. In these, a resolution of 82 eV was obtained at 17.7 keV, which is better by at least a factor of three than has been obtained with solid state detector systems. The energy range of the patterns was extended to 50 keV, corresponding to a minimum d-spacing of 1.18 Å. Unfortunately, data were not obtained from samples in the diamond cell.

In new tests completed at CHESS in February 1983, measurements on two samples were obtained over a range of pressures from 3 to 53 kbar using the lattice parameter of an internal standard (NaCl) to determine the pressure. Although low counting rates (due to extremely small sample volume) made it impractical to use the narrowest slit and obtain the highest resolution, the resolution achieved (170 eV at 17.7 keV) was comparable to that of the best solid state detector systems using synchrotron radiation, and was from two and one-half to five times better than that using a rotating anode or sealed-tube x-ray source. For the first time, the 002 and 110 reflections of tetragonal $\text{ZrO}_2 \cdot 18\% \text{CeO}_2$ were resolved at pressures up to 53 kbar to shed new light on phase relations for this material (see below). The lattice parameter of gold also was compared with that of NaCl at pressures up to 50 kbar, in preparation for possible use of Au as a pressure calibrant.

Low counting rates now limit the usefulness of the new diffractometer but a six-pole wiggler is being installed at CHESS, and comparable devices are being developed at other synchrotron sources. The result will be a six-fold increase in the photon flux at 10 keV, and perhaps as much as a hundred-fold increase at 50 keV. This would greatly enhance

the capability of the NBS instrument, whereas the energy dispersive method has already reached count-rate saturation and can benefit very little.

An additional application of the microdiffractometer is in obtaining x-ray diffraction data and x-ray fluorescence spectra from microscopic specimens or from selected areas of larger specimens. In anticipation of such applications, the microdiffractometer used at CHESS in February was equipped with a microscope mounted so that a selected specimen feature can be centered in the x-ray beam. The smallest collimator presently available gives a beam diameter of 30 μm , but a 12 μm collimator can be purchased. Unfortunately, there was no opportunity to perform the selected area diffraction experiment at CHESS because of synchrotron equipment failures which reduced the available beam time. A similar microscope has since been added to the energy dispersive system at NBS. Here, the only available collimator gives a beam of 150 μm in diameter. On both the instrument used at CHESS and the one used at NBS, the new microscopes are useful for rapid visual alignment of the diamond anvil cell.

Efforts to develop high temperature capability of the DAPC for application to ceramic materials are continuing. Part of this work involves improving the accuracy of pressure measurements at high temperature. It was demonstrated by numerical (computer) techniques that the temperature distribution in the DAPC is essentially isothermal when the heater is 1000 degrees above ambient. However, measurement of the shift of the ruby R1 fluorescence line is the principal means for determining the pressure in a DAPC. The wavelengths and widths of the R1 and R2 lines are strongly affected by temperature; and, at high temperatures, R1 and R2 overlap significantly. At low temperatures, an additive correction term is adequate to account for the contribution of temperature to the shift of the R lines; but, at high temperatures, the overlap of R1 and R2 introduces nonadditive uncertainties. Consequently, a detailed modeling of the full R1 to R2 lineshape, as a function of temperature and pressure, is under study and is nearing completion. A model for the lineshape, a hybrid of Lorentzian, Gaussian, and black-body components, was constructed. The model was found to work very well for the high temperature, one-atmosphere spectra. Additional room temperature, high pressure data were taken and are currently being analyzed in the context of the model.

Experimental Materials Research

Electronic Ceramics

ZrTiO_4 "doped" at various levels with SnO_2 is an attractive material for microwave resonator applications (see Subtask 1). A preliminary phase diagram for the ZrO_2 - TiO_2 system, figure 3, was redetermined and shows considerable complexity. ZrTiO_4 cannot be synthesized below $\sim 1125^\circ\text{C}$ using conventional blends of milled oxide powders or mixed hydroxide gels. The compound, including solid solutions, sluggishly decomposes below this temperature and undergoes a competitive reaction involving an order-disorder transition. A homogeneity region, $\text{Zr}_{1-x}\text{Ti}_{1+x}\text{O}_4$, is shown in figure 3, but, until recently, it was not clear whether this phase is

stable or transitory. To further understand the complex structural chemistry observed, neutron diffraction analyses were initiated in collaboration with A. Santoro (Reactor Division) and P. Burdot (CNRS, Grenoble, France; guest worker at NBS). The high temperature ($> 1125\text{ }^{\circ}\text{C}$), quenched form of ZrTiO_4 has the $\alpha\text{-PbO}_2$ structure-type with Zr and Ti cations disordered in one crystallographic position. A low temperature phase, $5\text{ZrO}_2 \cdot 7\text{TiO}_2$, was shown to have cation ordering according to $\text{Zr}_4(\text{ZrTi}_7)\text{O}_{24}$, equivalent to the columbite structure, $\text{Fe}_4\text{Nb}_8\text{O}_{24}$.

A range of $\text{ZrO}_2/\text{TiO}_2$ compositions were prepared from chemical precursors (see subtask 1) to help determine stability relations below $\sim 1200\text{ }^{\circ}\text{C}$ in the system. Initial crystallization of these materials at $650\text{ }^{\circ}\text{C}$ yields metastable, $\alpha\text{-PbO}_2$ -like phases from about 4/1 to 1/4 Zr/Ti content. With continued annealing below $\sim 1150\text{ }^{\circ}\text{C}$, the phases unmix to form monoclinic ZrO_2 or TiO_2 solid solutions plus a columbite-type phase which has ZrTi_2O_6 stoichiometry rather than $5\text{ZrO}_2 \cdot 7\text{TiO}_2$ as obtained from conventional preparations. It is concluded that ZrTi_2O_6 , with very limited solid solution, is the only stable low temperature phase in the system. It decomposes near $1150\text{ }^{\circ}\text{C}$ to TiO_2 plus disordered ZrTiO_4 solid solution. However, partly ordered $\text{Zr}_{1-x}\text{Ti}_{1+x}\text{O}_4$ variants as suggested in figure 3, can be stabilized by dopants such as Y_2O_3 , Ta_2O_5 , YTaO_4 , and MoO_3 . This indicates that improved compositions, especially, with high TiO_2 content, could be developed for dielectric applications. Additions of SnO_2 effectively inhibit transitions in ZrTiO_4 and lower the decomposition temperature.

Li_2O -containing phases are candidate solid electrolyte materials for lightweight, high energy battery systems. Neutron diffraction studies are in progress to elucidate mechanisms of Li^+ conduction in phases characterized by phase diagram work. The purpose of the work is to determine underlying structural features that influence conduction processes and, thereby, guide chemical synthesis research toward improved materials. During FY83, the crystal structure of the compound reported in the literature as " Li_4ZrO_4 " was solved. The phase diagram (see Annual Report, 1982) suggests that this phase is considerably richer in ZrO_2 . X-ray and neutron diffraction (Reactor Division) proved that the stoichiometry is $\text{Li}_6\text{Zr}_2\text{O}_7$. Ionic conduction in " Li_4ZrO_4 " was reported in the literature and shown to be an order of magnitude greater than that of Li_2ZrO_3 . However, the work did not distinguish between cation and anion conductivity. Possible conduction modes will be determined by neutron diffraction at $\sim 300^{\circ}$ and $\sim 600\text{ }^{\circ}\text{C}$.

Additional neutron diffraction studies were conducted in collaboration with A. Santoro (Reactor Division) and R. J. Cava (Bell Telephone Labs, guest worker). Most of this work involves transition metal oxides to which Li^+ is "inserted" using chemical precursors (D. W. Murphy, Bell Telephone Labs). The structures of Li_2ReO_3 , $\text{Li}_{0.36}\text{WO}_3$, and several anatase-based (TiO_2) compositions were refined and conductivity measurements are in progress at Bell Telephone Labs.

Toughened Materials

A possible route to improved mechanical properties of ceramics under current worldwide investigation is through transformation toughening. The toughening mechanism is achieved by controlled processing of submicron powders to yield a specific assemblage of crystalline phases in the densified ceramic that can transform in the stress field of a propagating crack and inhibit further crack growth. Thus, transformation toughening is inherently dependent upon phase equilibria relationships.

For example, zirconia-based ceramics are particularly suitable for toughening as ZrO_2 undergoes a martensitic (diffusionless) transformation involving monoclinic and tetragonal phases. By addition of a second component, such as Y_2O_3 , a partially stabilized zirconia ceramic can be produced containing the tetragonal form as intergranular precipitates in a cubic matrix. Stringent microstructural control is needed to satisfy the requirement for transformation toughening, namely that the tetragonal particles are metastable in the matrix at the operational temperature and that they transform to the stable monoclinic form in the stress field of the crack.

Conceptually then, the only thermodynamic and structural criteria necessary for transformation toughening are (a) a metastable phase, (b) a rapid transformation, and (c) a metastable phase with at least one crystallographic cell dimension smaller than the stable phase (i.e., volume expansion in, at least, one direction during transformation). These criteria can be met by thermal and/or pressure processing. Heretofore, all work in ceramic toughening has concentrated, with some success, on thermal treatments at ambient pressure to obtain the necessary stable/metastable phase assemblages. Noting that criterion (c) is an unusual condition for high temperature phases but is common for high pressure phases, further advances should be possible by consideration of the pressure variable. This means that the phenomenon of transformation toughening can be more general than previously considered and could lead to a new class of important materials; i.e., pressure toughened ceramics (PTC). Partially stabilized ZrO_2 is the first demonstrated case of transformation toughening in ceramics. It also is a ceramic with many applications ranging from heat engines to optical windows to sensors. Considering that ZrO_2 also undergoes transformations other than monoclinic to tetragonal, it may be amenable to the pressure toughening concept. However, the temperature-pressure diagram of ZrO_2 is not well established as contradictory results have been published. Studies in this subtask are concentrating on pure ZrO_2 and $\text{ZrO}_2(\text{CeO}_2)$ solid solutions.

Powder samples of the tetragonal form of $\text{ZrO}_2 \cdot 18 \text{ mol.}\% \text{ CeO}_2$ were studied by energy dispersive diffraction in the diamond anvil pressure cell (DAPC) to 15.5 GPa to measure compressibility and explore the possibility of a transition to the cubic form. The transition from the tetragonal to cubic form would be indicated by the merging of two overlapping diffraction peaks into one. Preliminary studies showed such an effect at approximately 2.8 GPa, and the cubic form was retained metastably by pressure quenching from a nonhydrostatic environment. However, due to the relatively poor resolution of the x-ray pattern, experiments were conducted with the CHESS synchrotron using the greatly

improved resolution of the wave length dispersive system (see above). These experiments showed two distinct lines at 5.2 GPa, indicating the tetragonal to cubic transition did not occur. A plot of the volume as a function of pressure shows a sharp discontinuity at approximately 9.5 to 10.5 GPa, indicative of a phase transition. The $\Delta V/V_0$ at this point is approximately five percent. The potential transition will be examined by optical microscopy by observing the birefringence changes in a single crystal. Attempts to grow single crystals are in progress.

At present, the P,T diagram of pure ZrO_2 consists of equilibrium and nonequilibrium data with conflicting phase boundaries. A detailed study of this diagram was initiated in the DAPC using both optical microscopy and energy dispersive x-ray diffraction. Optically, the transition in the 2.8 to 4.4 GPa is spectacular with changes in birefringence and fracturing of the crystal, particularly on the down stroke. At room temperature, on the upstroke, the transition pressure varies with the cycle; changing from approximately 4.4 GPa on the first cycle to about 3.2 GPa on the fifth cycle. On the downstroke, the transition always occurs at approximately 2.8 GPa. Experiments were carried out at 130 °C and 250 °C. The cycle effect for the upstroke greatly diminishes or disappears at the higher temperatures. However, the hysteresis between the transition pressures of the upstroke and downstroke remains. These preliminary experiments, carried out in a hydrostatic environment, indicate that $\Delta P/\Delta T$ is in approximate agreement with current data but is shifted to lower pressures by approximately 0.4 GPa.

Energy dispersive x-ray experiments are in progress to 16.1 GPa. The transition was determined to involve monoclinic to orthorhombic or tetragonal (II) variants. Before transformation, monoclinic ZrO_2 compresses very little with a $\Delta V/V_0 < \text{one percent}$. However, at the transition, $\Delta V/V_0 \sim \text{six percent}$. These experiments are continuing to higher pressures as it is possible that the currently accepted slope of the orthorhombic to tetragonal (I) phase boundary is incorrect and that this tetragonal form may be stable at room temperature in a higher pressure region.

Non-Oxides

Metglasses, Ni_3Al , and the explosive RDX were investigated using the DAPC. The radial distribution function (RDF) of the metglasses FeW (56 wt.% W) from Watervleit Arsenal and Ni-P from D. Lashmore of the Electrodeposition Group were determined and their bulk moduli calculated. The compressibility and bulk moduli of Ni_3Al and MAR-M200 were measured for Watertown Arsenal.

In cooperation with Picatinny Arsenal and the Naval Surface Weapons Center, methods were developed to measure and identify decomposition rates and processes in explosives, as a function of pressure and temperature. The pressure dependence of the thermal decomposition temperature of RDX was measured. With increasing pressure, there is a corresponding increase in the decomposition temperature, with the rate of increase rising rapidly above 30 kbar. Decomposition products detected by absorption spectra were tentatively identified as CO_2 , N_2O , and H_2 which, depending upon the pressure and temperature of formation,

may exist as solids, liquids, or gases. The measurement techniques, as developed for this wide variety of materials, are directly applicable to ceramics in future research efforts.

Evaluated Data--Production and Compilation Subtask 3

C. R. Hubbard

JCPDS--International Centre for Diffraction Data

Identification of phases in materials by XRD is by far the most widely performed analysis. The JCPDS--International Centre for Diffraction Data Research Associateship continues to produce highly accurate standard reference powder patterns in collaboration with NBS. A new agreement to formalize and strengthen the relationship between NBS and the JCPDS was drafted and is under final negotiation.

NBS Monograph 25, Section 20, was published in October 1983, and contains 65 experimental and one calculated pattern. Over two-thirds of the patterns are designated as "common phases". All of the experimental patterns were digitally recorded and interpreted with the aid of computer programs. During FY83, the lattice parameter refinement program was extensively updated, converted to FORTRAN77, and documented in an NBS Internal Report. This version allows batch or interactive input. It also can read the PKS file produced by the powder pattern processing programs. This automation of the interpretation process is partially responsible for the 30 percent increase in the number of reference patterns completed. The accuracy of the reference data also improved considerably.

The Research Associate members continue to be involved in other activities of the JCPDS-ICDD. M. Morris collaborated with the Forensic Subcommittee to collect a forensic subfile of the PDF. This subfile was announced in July 1983 and is expected to have extensive utility at state crime labs. N. Pyrros collaborated on the peak finding task group in an effort to determine which algorithms and data collection parameters lead to the most accurate 2 θ values. E. Evans continued her involvement in the Data Base Subcommittee, particularly on use of large numbers of calculated patterns for evaluation of the PDF.

The PDF is used in thousands of laboratories for phase identification. The file consists of over 40,000 patterns collected over a period of nearly 40 years. The quality of the reference patterns is very important in phase identification procedures. A five-year project by the JCPDS-ICDD, with assistance from NBS, is underway to critically reevaluate the entire PDF and to build a master magnetic data base. The joint Crystal Data-JCPDS evaluation program, AIDS, was (1) converted to FORTRAN77; (2) extensively expanded; and (3) used to process over 30,000 entries. The output was reviewed by W. Wong-Ng (JCPDS) and corrections to the master magnetic data base are beginning at both JCPDS-ICDD headquarters and at NBS. Plans are to complete the critical review and error correction by September 1984, at which time PDF improved indexes and search/match tapes will be produced from the master data base. To

support this effort, the JCPDS-ICDD has purchased a VAX-750 computer system and several input terminals for their headquarters. In addition, several terminals were also purchased by the JCPDS for use at NBS.

The critical review of new data entering the PDF also uses the evaluation/data base building program AIDS83. Approximately one-half of the editorial effort is performed by H. McMurdie (ceramics) and M. Mrose (minerals), who are members of the RA. M. Mrose joined the group in July 1983.

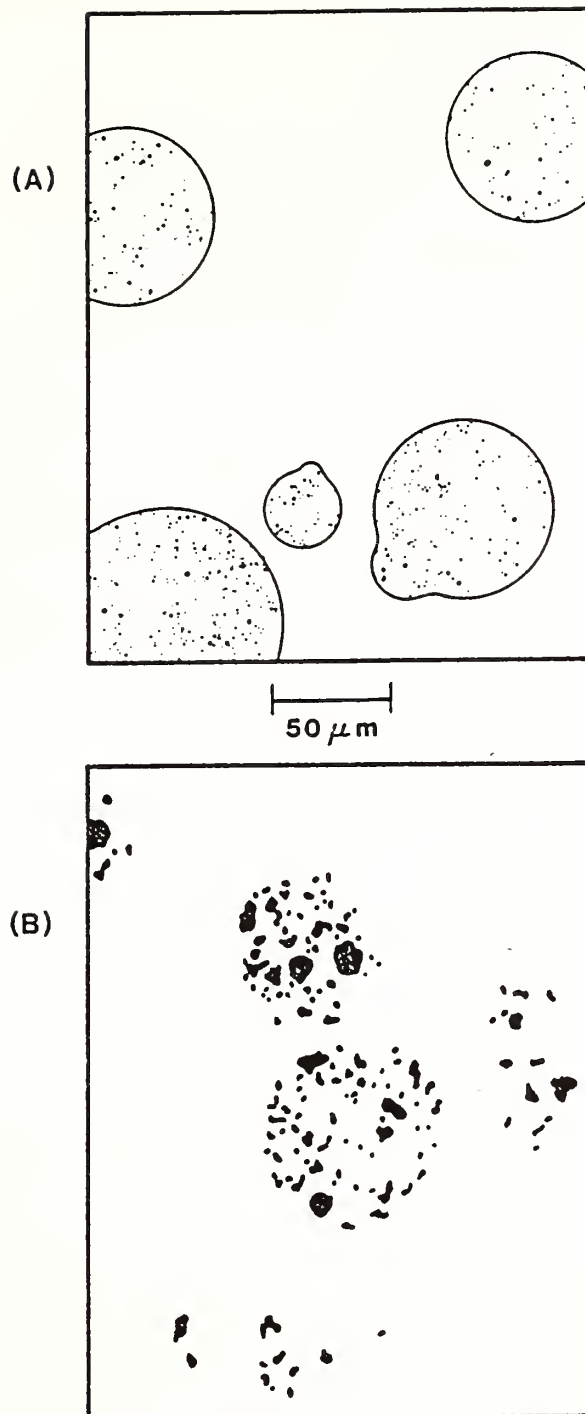


Figure 1 Line reproductions of SEM micrographs illustrating spherical agglomerates in green state MgAl_2O_4 (A) and generation of new pores (darkened) after densification at 1500 °C (B).

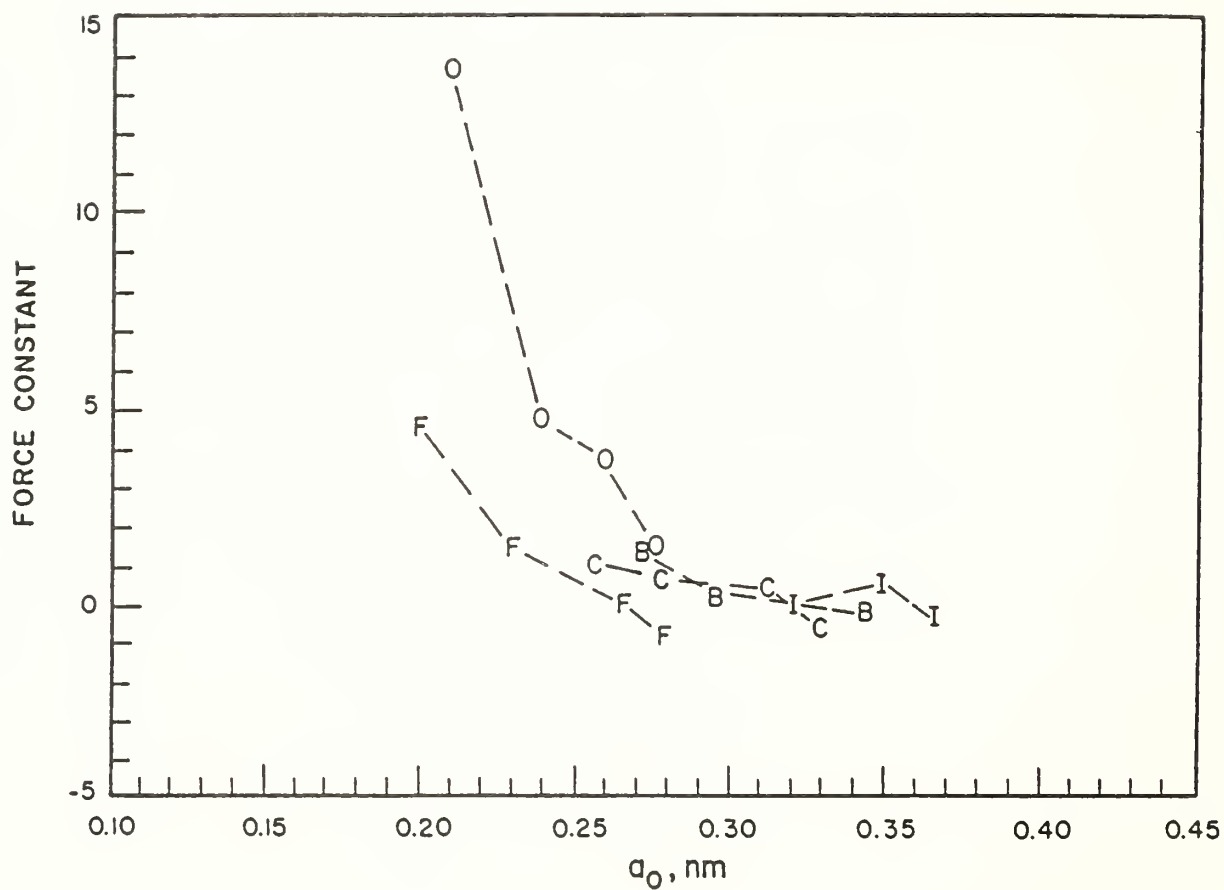


Figure 2 Force constant versus nearest neighbor equilibrium bond length, a_0 . The "Os" represent (with increasing a_0) MgO, CaO, SrO, and BaO; the "Fs," LiF, NaF, KF, and RbF; the "Cs," the alkali bromides; and the "Is," the alkali iodides.

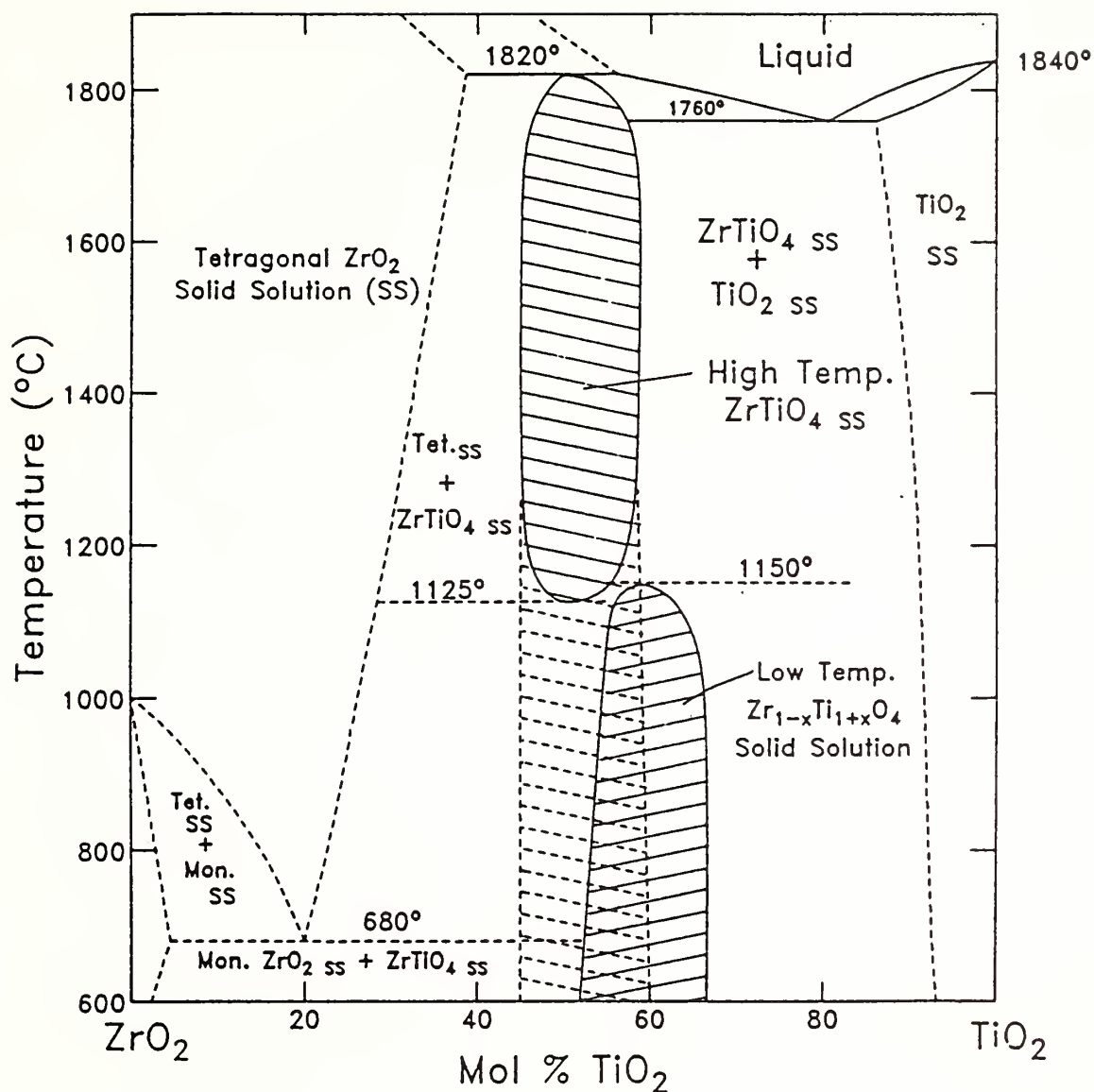


Figure 3 Preliminary phase relations in the vicinity of ZrTiO₄ superimposed on published data for the ZrO₂-TiO₂ system. Dashed lines from the ZrTiO₄ solid solution (ss) region represent phase metastability due to sluggish decomposition kinetics on cooling. The low temperature, Zr_{1-x}Ti_{1+x}O₄, homogeneity region mostly represents metastable phase relations but includes the stable compound ZrTi₂O₆.

Figure 1. A plot of the rate of reaction, k_{obs} , versus the concentration of the reactant, $[A]$, for the reaction of A with B in the presence of a catalyst C . The reaction is first order in A and zero order in C . The rate of reaction is constant for a given concentration of A and increases linearly with the concentration of A . The rate of reaction is independent of the concentration of C .

3.2 HIGH TEMPERATURE MATERIALS CHEMISTRY FOR PROCESSING AND DURABILITY

The objective of this task is to provide a general high temperature chemistry measurement science base for advanced/substitute/conventional materials processing (e.g., ceramic and glass) and service behavior in extreme environments (e.g., hot corrosion, slagging, and defense applications). This objective is accomplished through, development of new or improved experimental methods, their application to determination of basic data and new concepts, and through modeling of ceramic/metal gas-liquid-solid equilibria, together with critical evaluation- compilation of ceramic phase equilibrium diagrams. The latter activity results in the periodic publication of Phase Diagrams for Ceramists (PDFC), volumes which currently emphasize systems containing oxides, sulfides, sulfates, halides, C- and N-containing compounds, and involve solid, liquid, and gaseous species.

Molecular-specific experimental methodologies and theoretical modeling tools are being developed and applied to the determination of basic thermochemical and kinetic data and chemical mechanisms for interactions of ceramics, and glasses with aggressive gaseous high temperature processing and service environments. These methods primarily emphasize the identification of molecular species, together with accurate measurement and model predictions of their concentration, spatial, and temporal distribution in high temperature vapors and gases, and in the presence of complex solid or liquid phases. The related in situ measurement problems of temperature and flow (gas phase) are also addressed by this task. In support of phase diagram determinations, and for completion of thermodynamic cycles in gas-solid-liquid equilibria, the characterization of condensed phase composition and structure is achieved by x-ray diffraction, electron microscopy, and electron spectroscopy for chemical analysis (ESCA). The work of this task is described here under five subtasks: (1) Phase Diagrams for Ceramists Data Center; (2) Vapor Transport Thermochemistry; (3) Characterization of High Temperature Gaseous Environments in Processing and Service; (4) Data Center on Materials and Components for Fossil Energy Applications; and (5) High Temperature Thermophysical Properties.

The results of this work are used by industry and other government agencies for (a) performance predictions and test method development in new high technology applications such as coal-combustion and conversion and advanced propulsion systems, and (b) to support materials processing at high temperatures including chemical vapor deposited coatings, and ceramic, glass, and metals processing. In addition to base program support, the task addresses other NBS program and other agency needs, including those of the Office of Standard Reference Data (OSRD) (phase diagram evaluation/compilation), DOE-Fossil Energy (alkali vapor transport), Army Research Office (ARO) (alkali chemistry in flames), NASA (levitation calorimetry of liquid tungsten), DuPont-DOE Savannah River (vaporization of nuclear waste glass), Office of Naval Research (ONR) (stored chemical energy propulsion), Bell Laboratories (glass optical fiber processing), Air Force Office of Scientific Research (AFOSR) (laser-materials interaction mechanisms), Defense Nuclear Agency (DNA) (boron nitride-composite

vaporization), and DOE-Laramie (data book on materials for fossil energy). An expanded effort in the Phase Diagrams for Ceramists activity is expected in FY85 with new support arising from the American Ceramic Society (ACerS) through Industrial-Government sources.

FY83 Significant Accomplishments:

- o An agreement between the American Ceramic Society and NBS was completed formalizing the long-standing collaborative effort in the compilation, critical evaluation, and publication of phase diagrams for ceramic systems. Auxiliary to this agreement was the development by NBS, with ACerS approval, of a five year expansion/funding plan for the Phase Diagrams for Ceramists Data Center.
- o Final editing, formatting, and word processing codification was completed for Volume V of Phase Diagrams for Ceramists with the material submitted to the American Ceramic Society for publication. This volume contains 663 critically evaluated phase diagrams, current to 1976, of halide, sulfide, oxynitride, aqueous, and ceramic-gas systems.
- o The theory of mixing for complex ceramic solid and liquid phases, developed under this Task, has been extended to include systems containing Na_2O , MgO , FeO , Fe_2O_3 , Fe_3O_4 , and their compounds. In combination with our previously established model data base for K_2O , CaO , Al_2O_3 and SiO_2 , these new components provide an essentially complete data base for phase equilibria modeling of coal slag, glass, and many other ceramic and mineral systems important in ceramic processing and application.
- o The vapor transport thermochemistry of a nuclear waste glass, based on the DuPont Savannah River process, was established quantitatively and the results provide a basis for new process development. The results indicate that careful control of B_2O_3 activity and temperature is needed to reduce unwanted vapor transport of the Cs radionuclide.
- o The vaporization and mixing thermochemistry for several GeO_2 - SiO_2 fiber optic (for telecommunications) glasses was established and the results provide a basis for new glass processing models. Industrial model assumptions of thermodynamic equilibrium and near-ideal mixing were shown to be oversimplified.
- o The melting enthalpy for tungsten (53.1 ± 1.3 kJ/mol at 3695 K) was determined for the first time using a unique levitation calorimetric approach. This result represents the culmination of several years of collaboration between NBS-GE-Rice University under NASA's materials processing in space program.
- o Serious long-standing discrepancies in the vaporization thermochemistry of liquid KOH were resolved using the unique transpiration mass spectrometer facility. The new results will greatly modify predictions of alkali vapor transport in areas such as glass and ceramic processing, as well as fluidized bed combustion and magnetohydrodynamic power generation.

Phase Diagrams For Ceramists Data Center

Subtask 1

J. W. Hastie, L. P. Cook, H. M. Ondik, M. A. Clevinger, D. McKenna,
P. K. Schenck

NBS has a well-established NBS role in the critical evaluation, compilation, and dissemination of phase diagrams for use by ceramists. This is a joint activity with the American Ceramic Society. The work is closely coupled with current needs as perceived by NBS and an ACerS advisory committee. Recent activity in this area has been expanded in response to the increased complexity and quantity of new phase diagrams, together with an expanded dependence by industry and others on critically evaluated diagrams and related thermodynamic data. Figure 1 reflects the exponential growth in the number of ceramic phase diagrams published and evaluated (by NBS) over the past half-century. The total number of literature diagrams is estimated to be 20 percent greater than for the compiled/evaluated numbers given in the figure. According to the terms of the recently signed agreement between NBS and ACerS and the associated a five year expansion plan, resources for an expanded phase diagram data base activity will be provided jointly by Industry, NBS, and other Government agencies.

Key elements of current data center activities include: (a) Evaluation and Production, leading to publication by ACerS of the Phase Diagrams for Ceramists (PDFC) book series; (b) Data Base Development, with emphasis on computer control; (c) Modeling/Optimization, in support of the critical evaluation activity; (d) Experimental, to maintain evaluative competence, improve measurement techniques, and to be responsive to specialized needs for new phase diagram data. Other Group activities have also been focused on the needs of the Data Center, particularly in support of the modeling and experimental functions. In addition, the Contributing Editor program (with academic, industrial, and international experts) has been expanded and also includes, for selected systems, coupled thermodynamic--phase diagram model evaluations. Coordination of new Data Center plans with those of the ASM-NBS alloy (located in Division 564) and the Society Plastic Engineers-National Bureau of Standards (SPE-NBS) polymer (Division 563) counterparts has also been implemented. These combined NBS phase diagram Data Center activities and plans are detailed in the report Phase Diagrams in Materials Science.

(a) Evaluation/Production. A major Data Center output is the publication of PDFC books, beginning with Vol. I in 1964, with Vol. IV being the most recent publication (1982). These volumes contain critically evaluated phase diagrams together with commentary and bibliographic information. During the past year Vol. V was completed and submitted to ACerS for publication in 1983. This volume, edited by R. S. Roth, T. Negas, and L. P. Cook, contains 663 new diagrams of halides, halides with other substances (especially metals and oxides), sulfides, oxycarbides and oxynitrides, aqueous systems, systems with CO₂, and ceramic-gas (primarily C-O-H) systems.

Considerable progress has also been made in the preparation of Volume VI (oxides) and Volume VII (including halides and sulfides) which will each contain about 2000 phase diagrams. Approximately 75 percent of the literature for Volumes VI/VII is in the critical evaluation process and an anticipated publication date for Volume VI is 1986. A cutoff for inclusion of literature in these volumes will be approximately January, 1983 (Chemical Abstracts date), with the result that the bulk of literature through 1982 will be covered.

A substantial change from previous practice has been made with regard to the organization of these volumes. All systems containing oxygen as a component (regardless of whether they contain dominantly halides, sulfides, etc.) will be placed in Volume VI. Also, Volume VII will be the first to contain thermochemically optimized phase diagrams. These diagrams will represent computer-drawn "best-fits" to available phase diagram and thermochemical data, and will include experimental data points for comparison along with a detailed thermochemical critique.

(b) Data Base Development. A major objective of the Data Center, central to the NBS-ACerS five year plan, is to convert to full computer control the manual operations used for the preparation and production of phase diagram compilations. The data base organization necessary to achieve this objective is basically as follows: (1) a bibliographic file containing primary bibliographic information as well as chemical descriptors and keywords; (2) a file of graphical data containing the phase diagrams in both unedited (as published) and edited or optimized versions; (3) a file of experimental critiques (text subfile); (4) a file of optimized Gibbs free energy functions to be used for computer calculation of the phase diagram, and a thermochemical critique (text subfile). At present it is planned to utilize existing thermochemical data bases, rather than to develop an independent thermochemical data base. However it may be necessary to create specialized data files for some systems, especially those containing solutions as there is no central source of data on ceramic solution activities. Existing data bases will be used for crystallographic data. The data base will also contain what may be regarded as a software file, containing programs designed to provide links among the other four files, manipulate their data, and produce desired output for dissemination. An important component of this software file will be programs for the calculation of phase diagrams, modeling, optimization, and extrapolation.

Significant progress has been achieved in the past year in software and protocol development for the first two files, bibliographic and graphical. The bibliographic file system, developed in collaboration with the Office of Standard Reference Data (C. Messina), is near completion and will be used to prepare Vol. VI of PDFC. A very efficient prototype graphics system has been developed and tested on representative ceramic phase diagrams. In the near term, the refined system will be applied to the digitization, computer storage, editing, and camera ready production of select groups of diagrams in Volume VI of PDFC. The figures 1-4 presented here were produced with this graphics system.

(c) Modeling/Optimization. Computer modeling of ceramic phase diagrams can enhance or "optimize" experimental phase diagram data, particularly

when coupled with associated thermochemical data such as mixing enthalpies, compound free energies of formation, and solution activities. Development of computer models is essential to the long range goal of computer-aided critical evaluation and production of ceramic phase diagrams. At the present time three groups within Division 561 contribute to this effort. These three activities focus on: application of molecular dynamics theory to phase diagram prediction (R. Munro), use of cluster variation methods for the prediction of phase transitions (B. Burton), and, the development of solution models for phase diagram optimization and prediction (this Task). Description of the first two activities is given elsewhere in this report and the present discussion deals with the solution modeling problem.

In principle, phase boundaries and thermodynamic functions such as Gibbs energy are interrelated. However, specification of a single phase boundary point on the liquidus curve of a phase diagram requires both temperature and composition to be fixed. For the complete thermodynamic construction of a phase diagram the Gibbs energy of each phase is required as a function of temperature and composition. Such analytical expressions can be derived provided a solution model is assumed, which essentially is a thermodynamic relationship between activities (or apparent mole fractions) and nominal mole fractions for the mixture components. Well-known examples of solution models include, ideal, regular, and the molecular-level associated liquid or clustering models. Models of this type have been useful for coupled thermodynamic--phase diagram optimization analysis of select binary alloy and molten salt systems. However, for typical ceramic systems the available models do not appear to be applicable owing to the substantial thermochemical interactions that occur on mixing. Development of new strong-interaction solution models for ceramic systems is therefore needed. In addition to allowing for thermochemical optimization of experimental phase diagrams, such models also form the basis for converting phase diagram information to useful vapor pressure data and vice-versa. Also, in some cases, such as the ideal mixing of complex phases model developed under this Task, phase diagram predictions appear feasible for systems where no experimental phase equilibria data exists.

The utility of even sparse experimental phase diagram data can, in principle, be greatly enhanced through thermochemical optimization techniques. Success in this area for ceramics has been limited to a relatively few simple systems which exhibit regular solution behavior, such as molten salts. A key part of the long range NBS-ACerS plan is to expand the application of this approach to as many ceramic systems as possible. The PDFC Data Center, together with Office of Standard Reference Data (OSRD), has recently initiated several pilot projects in this area with emphasis on new model development.

During the past year a successful model to predict solution activities and vapor pressures in binary and higher order systems containing compounds (solid and liquid) of K_2O , Na_2O , CaO , MgO , Al_2O_3 , SiO_2 , FeO , Fe_2O_3 , and Fe_3O_4 has been developed. This model has a thermodynamic basis and does not rely on an assumed molecular structure of the liquid phase, or on experimental information such as mixing thermochemistry. Extension of the model to include phase diagram predictions is planned. As an example

of the validity and utility of the model, consider the highly complex system of calcined dolomitic limestone. The sample composition and model predictions are summarized in Table 1. Item B shows the predicted distribution of the component oxides in the solid and liquid phase. The identity and composition of predicted solid phases is listed under item C. Items D and E indicate the hypothetical model liquid components and their concentration as determined by free energy minimization. According to the model theory, these mole fraction quantities may be taken to represent activities of the various components. The thermodynamic relationship between activity and partial pressure allows one to calculate partial pressures from these activity data. Figure 2 shows excellent agreement between the alkali partial pressures predicted by the model and the experimental results. Note that only the lowest temperature Na-data points are valid for this comparison owing to a decreased substrate Na-content with increased temperature. Similar comparisons have been made with other dolomite compositions, and with glasses, coal slags, and molten salts, indicating wide applicability of the model.

The model has attracted considerable interest in industry and other laboratories for diverse applications. Already, the following establishments have expressed an interest in utilizing the computer program, data base, and related material: DOE-Morgantown (slag modeling); DuPont-Wilmington (glass-metal wetting); A. Cooper-Case Western Reserve (diffusion in glass); DuPont-Savannah River (nuclear waste processing); PPG-Pittsburgh (fluoride glass volatility in fiber production); CSIRO-Sydney (fluidized bed coal-slugging); New South Wales Electricity Comm.-Australia (steam plant design for high slagging coals); St. Gobain-France (glass processing); and Oak Ridge National Laboratory (MHD slag thermochemistry). Also, Dr. N. Christensen of F. L. Smith and Company (Denmark) has pointed out that this modeling activity is important to the prediction of corrosive alkali vapor transport and deposition in cement processing.

In principle the model should also permit calculation of phase diagrams and this aspect is under investigation. One should stress, however, that the viability and reliability of this model require continued testing as additional components are added to the database. Thus this closely coupled experimental [see item (d) below] and modeling effort will be continued in FY84 for optimum development and public dissemination of the model.

(d) Experimental. Experimental research performed in support of the Data Center program includes both classical determination of phase diagrams (i.e., direct phase identification) and indirect measurement based on Gibbs energy relationships. In the latter case use is made of vapor pressure measurement using unique NBS facilities, as discussed under Subtask 2. These thermochemical measurements of phase equilibria are particularly useful for testing solution models under development for phase diagram optimization and prediction, as discussed above under item (c).

During the past year a new project has been initiated in response to basic data needs of the Office of Naval Research (ONR)--Garrett Corporation development of stored chemical energy propulsion systems. The

system of interest is based on the exothermic reaction of a Li/Al alloy with H_2O (steam) to yield $Li_2O-Al_2O_3$ phases and H_2 (to be burned for additional thermal energy). Phase equilibrium data, needed for process design by Garrett, are virtually unknown for this system. This is an exceptionally complex system and a concerted experimental and theoretical effort is underway combining the expertise of three Groups within Division 561. Current effort is focused on a determination of phase equilibria in the system $Li_2O-Al_2O_3$. In addition to the 1:1 compound of principal interest, $LiAlO_2$, solid state and melting relationships involving this compound and Li_2O , Li_5AlO_4 , Li_3AlO_3 , $LiAl_5O_8$, and Al_2O_3 are under determination. This activity is closely coordinated with measurement of vapor pressures by thermogravimetric analysis and Knudsen effusion mass spectrometry.

Vapor Transport Thermochemistry Subtask 2

J. W. Hastie, E. R. Plante, D. W. Bonnell, A. B. Sessoms

This subtask develops and applies new or improved measurement techniques to the molecular-level analysis of vaporization processes for high temperature solids (e.g., ceramics) and melts (e.g., coal slags, glasses, and salts) in process atmospheres containing reducing, oxidizing, carbonated, halogenated, sulfated, and hydrous components. These conditions and the data obtained are generic to high temperature process environments, and particularly those where hot corrosion and high temperature oxidation are material-limiting factors. For example, in the developing technology of pressurized fluidized bed combustion (PFBC), removal of coal and dolomite-derived alkali (Na and K-containing species) impurities to a gas stream concentration level below 0.02 ppm is necessary to control hot corrosion of turbine blades in PFBC. NBS participation, at DOE's request, in the DOE-Morgantown Energy Technology Center Research and Development program on particulate and alkali control in coal combustion process streams, provides for close interaction and technology transfer with industrial participants, particularly General Electric, Westinghouse, the Electric Power Research Institute, Exxon, and a number of relatively small air pollution technology companies. NBS expertise in this area has also led to a recent request, and a formal collaborative program, by the DuPont Atomic Energy Division for NBS to carry out vapor transport measurements over simulated nuclear waste glass materials. These data are urgently required for the design of process conditions to isolate nuclear waste in glass materials.

In cooperative work with DOE sponsors, the recent measurement focus has been on ceramic, coal slag, and glass systems in atmospheres typical of coal gasifiers (CG), and pressurized fluidized bed combustors. Other cooperative projects involve oxides in reducing atmospheres (Navy-Garrett), BN-SiO₂ composites in very high temperature low-pressure oxidizing atmospheres (Defense Nuclear Agency), graphitic materials in low pressure neutral atmospheres (Air Force), and GeO₂-SiO₂ fiber optic glasses in neutral atmospheres (Bell Labs). These extreme conditions have required continued development of the transpiration (TMS) and modulated molecular beam Knudsen effusion (KMS) mass spectrometric techniques. Complementary efforts in data-base (solution activities, species Gibbs energies,...)

acquisition and computer modeling also constitute an integral part of this extreme-environment characterization effort. For most of the coal conversion and combustion systems of interest, the chemical state of Na- and K-containing species represents a pervasive theme in our understanding of the high temperature processes and of materials durability problems (e.g., in CG and PFBC). Examples of recent experimental and modeling activities pertinent to these problems are summarized below.

(a) Alkali Control in Combustion Atmospheres. Dolomitic limestone is used for sulfur retention in fluidized bed combustors. However alkali impurities in the limestone, together with the neutralizing effect of this basic material on alkali-containing coal mineral impurities (e.g., illite), can lead to excessive alkali vapor transport and corrosion of downstream components. To determine whether alkali vaporization from dolomite itself will exceed the tolerance (to hot corrosion) limits for turbine gas streams vapor pressure data have been obtained, as shown in figure 2. The good agreement between the TMS and KMS data is noteworthy. The several order-of-magnitude difference in characteristic residence times for these two techniques suggests that the system readily achieves thermodynamic equilibrium. Note that at the temperatures expected of PFBC operation (> 1200 K) the (Na+K) alkali pressure is above the turbine tolerance limit of 0.02 ppm (1.5×10^{-7} atm).

Even higher alkali pressures are likely in the combustor owing to the interaction of dolomite with alkali-containing coal minerals and with the H_2O and HCl gases present. For instance, in the presence of combustion atmospheres, these alkali vaporization rates will be enhanced by reaction with steam to yield the hydroxide species KOH and $NaOH$. Thermodynamic computer models are in increasing usage by process design engineers for the prediction of the likely concentration of these species. However, the thermodynamic data base for KOH is particularly suspect owing to the widely disparate literature data. Using the TMS method we have obtained new, accurate thermodynamic data, including Gibbs energies, enthalpies, and entropies of formation, for the vapor species KOH , $(KOH)_2$ and KO_2 .

(b) Nuclear Waste Glass Processing. Industrial and DOE plans for nuclear waste storage require the waste to be incorporated into a borosilicate glass. Vapor pressure data are needed for these glass-waste forms in order to optimize the process conditions (e.g., temperature, composition) and minimize losses of radionuclides by vapor transport during the high temperature mixing processing of the wastes. The primary objective of the present study was to define the vaporization thermodynamics of a simulated nuclear waste borosilicate glass, containing non-radioactive isotopes, as prepared by DuPont-Savannah River. Also, measurements of partial pressures for each vapor species allowed thermodynamic activities and related partial molar functions to be derived. Such basic data are pertinent to the development of thermodynamic models of other nuclear waste properties such as leaching and storage durability. Special emphasis was given to vapor species containing the following elements which in actual nuclear waste form are highly radioactive: Cs, Sr, Ru, and Re--present as a technetium simulant.

Alkali metaborates were observed to be the dominant vapor species and typical experimental data, obtained by the techniques of transpiration

and Knudsen effusion mass spectrometry, are given in figure 3. Note the excellent agreement obtained between the two techniques. These results indicate that for the proposed glass processing conditions ($\sim 1100^\circ\text{C}$) significant alkali vapor transport will occur.

(c) Glass Optical Fiber Processing. The rapidly growing technology of optical communications, using optical fibers, relies heavily on composition control during the $\text{GeO}_2\text{-SiO}_2$ glass-forming process. Consequently, industry is actively pursuing computer models relating the key processing factors to the composition of the final product. NBS assistance has been requested (Bell Laboratories) to provide the basic thermodynamic data needed to model the commercial modified chemical vapor deposition process (MCVD). Partial success has been achieved (by industry) in thermodynamic computer modeling of this process. Specifically, the relatively inefficient incorporation of GeO_2 into the glass has been demonstrated using estimated glass-mixing Gibbs energy data. However, the quantitative prediction of GeO_2 -glass concentration is strongly dependent on these estimates, and actual experimental data for the Gibbs free energy of formation of the glass are urgently needed. The present approach to obtaining these data is by measurement of the vapor pressure of GeO and O_2 over solutions containing GeO_2 dissolved in SiO_2 .

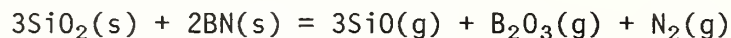
Measurements were made on $\text{GeO}_2\text{-SiO}_2$ samples provided by Dr. Robert Laudise and Dr. Kenneth McAfee of Bell Laboratories using the Knudsen effusion-modulated beam mass spectrometry system. Typical results are given in figure 4. The unusual form of these curves is characteristic of a very slow rate of diffusion of GeO_2 through the $\text{GeO}_2\text{-SiO}_2$ glass at temperatures below 1970 K . Also, the initial GeO pressures observed, which are high in comparison with those based on an ideal solution, indicate either positive deviation from Raoult's law or, with less likelihood, a combination of errors in tabulated and/or experimental data. This tendency for unmixing, together with a low GeO_2 diffusion rate, may explain why industrial attempts to prepare preforms by direct reaction of mixtures of GeO_2 and SiO_2 were unsuccessful. Presumably, the slow diffusion of GeO_2 could be a crucial step in the preparation of preforms by the MCVD method but may be avoided because of the simultaneous deposition of GeO_2 and SiO_2 in the "soot" prior to the consolidation step.

In the Knudsen effusion method, the rate of diffusion of GeO_2 is much too slow to obtain solution equilibrium data with any degree of confidence. Future experiments will therefore attempt to observe GeO pressures at higher temperatures where a closer approach to equilibrium is expected. Also, planned use of the TMS approach, with its longer gas residence times, will improve the prospects for equilibrium. The present results do suggest, however, that the key assumptions used by industry to model the glass forming process, namely thermodynamic equilibrium and near-ideal mixing of GeO_2 and SiO_2 , are suspect.

(d) Stored Chemical Energy Propulsion. Mass spectrometric measurements of vaporization and solution activities have been initiated in support of the recently implemented project on phase equilibria in the $\text{Li}_2\text{O-Al}_2\text{O}_3$ system (see Subtask 1). The results will allow for phase diagram construction using both the classical and Gibbs energy approaches. Also, the

activity data, obtained as a function of temperature and composition, will aid in developing thermodynamic models of the heterogeneous reactions involving H_2O and H_2 .

(e) Reentry Window Materials, Thermal Stability. Ceramic microwave transmission windows on atmospheric reentry space vehicles suffer from a communications blackout due to the high temperature effects of increased electronic conductivity in the window and, possibly, also in the vapor boundary layer. In support of defense needs for basic data and mechanistic understanding of the thermal and electrical degradation process, mass spectrometric measurements have been initiated on the vaporization behavior of BN-SiO_2 composite window materials. Preliminary results indicate significant thermal degradation over the temperature range 1600 to 2000 K with vapor pressures of SiO , B_2O_3 , and N_2 in the range 10^{-6} to 10^{-4} atm. The vapor species stoichiometric balances are consistent with the overall reaction:



However, the pressures are about an order of magnitude below the maximum thermodynamic values for this process. Further studies are planned to identify the rate limiting factors in this reaction.

Characterization of High Temperature Gaseous Environments in Processing and Service Subtask 3

P. K. Schenck, J. W. Hastie

Objectives of this Subtask are to develop and optimize measurement techniques for characterizing high temperature gaseous environments, including flames and laser induced plasmas, and to apply the methodology to mechanistic studies of materials processing and performance in those environments. During FY83, further refinements have been made to several new diagnostic techniques for application to mechanistic studies of combustion modification, including flame and smoke retardance, and for ceramic processing from high temperature vapors. These techniques rely on laser excitation of electronic states in atoms and molecules. The effect of enhanced thermal ionization of laser excited atoms (the optogalvanic effect or laser enhanced ionization) is used to modify the neutral/ion ratio from which species flow velocity and diffusion parameters are determined.

In collaboration with the Center for Analytical Chemistry, modeling and experimental studies have continued through FY83 on the collection mechanism of ions and electrons from laser enhanced ionization (LEI). Maximum sensitivity is obtained when a water cooled probe is inserted in the flame to collect the signal produced by electrons and ions formed by LEI using pulsed lasers. This sensitivity is explained by the near unity collection efficiency possible if the laser beam producing the electrons and ions is within the cathode sheath formed by the background flame ions around the probe (held at a negative potential with respect to the burner body or anode). The reason for this effect has been verified using a computer model for the behavior of the charge

distributions and electric field dependence inside the flame. The computer animation produced by the model demonstrates that the electrons rapidly move toward the sheath edge if formed near the cathode, while the ions, with 200 times lower mobility, remain stationary. This rapid separation of the laser produced charges forces the sheath edge to relax toward the burner (anode) resulting in a flux of current into the burner head which gives rise to the LEI signal. Further modeling to study the role of flame additives and probe geometry is planned.

In a separate study, an apparatus based on a krypton ion laser pumping a near-IR dye laser has been assembled to map potassium atom concentrations in normal and inhibited K seeded flames. This work is in support of Army needs for improved mechanistic understanding of Secondary Flash Suppression. The IR dye laser will allow us to monitor K concentration either by absorption or LEI (to the ppb level). Temperature measurements are planned using a computer controlled Raman spectroscopy and a fiber optic thermometer developed elsewhere at NBS. Efforts are underway to couple these experiments with the high pressure sampling mass spectrometer for simultaneous measurements of temperature and species concentration.

In addition, preliminary laser ablation tests have been made on carbon (graphite) and boron nitride refractory materials. The goal of this program is to characterize, by optical and mass spectroscopic techniques, the molecular processes occurring in plasmas resulting from surface ablation by high powered pulsed and continuous lasers.

In support of the new NBS Laser Processing Laboratory for ceramic materials, a design has been prepared for potential diagnostic techniques, including optical and mass spectrometric. Planned for the facility are real time spectrographic (species) and pyroelectric (temperature) measurements during the laser processing. Other techniques involving laser diagnostics will be studied for their applicability in laser processing research. This work, performed in conjunction with the Ceramics group, which will operate the new facility, will continue in FY84.

Data Center on Materials and Components for Fossil Energy Applications Subtask 4

H. M. Ondik, B. W. Christ¹

¹Division 562

The Fossil Energy Materials and Components project supports DOE Fossil Energy R&D needs by providing a central source of evaluated data on the properties and performance of materials and components in fossil energy systems. Particular emphasis is given to corrosion, erosion, and mechanical property data for metals and ceramics tested under coal conversion conditions. Materials properties and testing performance data are evaluated and compiled for construction materials intended for coal conversion use. The primary source of data is the library of DOE materials research contractor's reports. In addition, materials and components plant performance data are evaluated and compiled by the staff of the Fracture and Deformation Division (562) from reports of materials and component failures submitted to DOE on a voluntary basis by the various

coal conversion pilot plants. These two data bases are combined in the form of a periodically updated book, Construction Materials for Coal Conversion--Performance and Properties Data, NBS Special Publication 642, first published in September 1982, (800 pages). The book is produced as sets of pages numbered such that sections of the book are independent and can be updated and revised readily. By April 1983, the Government Printing Office had sold over three hundred copies and requested four hundred more to fill projected orders. The Inorganic Materials Division has responsibility for compilation of the basic set of data and also the analysis and discussion of the refractories information. The Fracture and Deformation Division (B. W. Christ and others) has responsibility for analysis of the metals and alloys data, as well as for the discussion of component failures which were largely concerned with metal components.

The first issue of the book focused on plant materials data for coal gasification, as this form of coal conversion provides the largest body of materials data. The data include information gained in practical plant experience, as well as the results of the materials research and testing programs. It deals with the information in the context of nine separate component areas of the coal gasification plant. The data applicable for a component area are summarized and discussed under that heading. The detailed results of the research and testing programs are included in a separate section which is divided into four parts covering the major performance and properties investigated in these programs. These four sections are headed:

- (1) Corrosion Effects, Chemical Reactions, and Phase Changes;
- (2) Erosion, Erosion/Corrosion, and Abrasion Effects;
- (3) Mechanical Properties Testing; and
- (4) Physical Properties Testing.

Each of these sections is divided into subsections for alloys, ceramic refractories, and, where such data exist, for coatings. A detailed index to the book lists the materials covered grouped by type. For metals, typical categories are stainless steels, cobalt-based alloys, carbon steels, etc. For refractories, the groupings first list the industrial categories--bricks, castables, etc.--and then the composition. For each material, the various properties are given for which data appear in the book, followed by the section reference and page. The index allows for location of testing and properties data for specific materials.

Current activities include preparation of two supplementary publications. The first of these, due in October 1983, will update the sections of the book to include data up to January 1, 1983, and also include data for materials under consideration for coal liquefaction use. The organization and table of contents of the book will be expanded to include component areas unique to coal liquefaction plants. It is expected that this first supplement will be concerned largely with alloy data. The second supplement due about April 1984, will bring the refractories data up to date, probably to January 1, 1984.

High Temperature Thermophysical Properties

Subtask 5

D. W. Bonnell

A joint experimental effort between NBS, Rice University, and the General Electric Company's Space Facilities Laboratory, has been in progress for several years. This effort, with support of the NASA Materials Processing in Space program, focusses on technique development and application to thermophysical property measurement, including heats of fusion, heat capacities, and enthalpy increment functions for extremely refractory materials such as tungsten. High temperature heats of fusion, enthalpy functions and heat capacities (C_p) are essentially unknown for third row transition metals, and other refractories with melting points above 2000 K. Theory has no predictive capability for these data, particularly for phase transitions, e.g., the change in C_p , solid to liquid, or the value of C_p near the melting point. There is not even a satisfactory explanation for why $C_p(l)$ is constant for metals and is generally much larger than the equipartition limit, $3R$ ($R = 8.314 \text{ J/g}\cdot\text{mol}$). Data obtained from these measurements are used in thermodynamic modeling of high temperature behavior of materials (phase diagrams and stability calculations), important for predicting performance of metals and ceramics at very high temperatures (greater than 2000 K) and improving process design. This effort utilizes electromagnetic levitation for containerless support of the refractory metal, and an electron beam gun to provide additional energy for melting. A conventional isoperibol (drop) type calorimeter has been modified to accept samples dropped from the levitation region to measure their heat content. For temperature measurement, use is made of a GE-designed silicon diode matrix video camera which has the additional circuitry and optics necessary to permit its use as a spectral radiance pyrometer.

Recent research has concentrated on tungsten, and a significant effort has been devoted to solving the problem of retaining melting tungsten until the phase change is complete, and then successfully capturing the molten sample with the calorimeter. This activity has finally yielded the first direct determination of the heat of fusion of tungsten, $53.1 \pm 1.3 \text{ kJ/mol}$ at 3695 K. Efforts are underway to improve the statistical uncertainty of this value, and to obtain heat content data of the liquid for a range of temperatures above the melting point. A successful effort was recently made to levitate molten tantalum, but this liquid, as expected, is much more difficult to contain and the data obtained are still being evaluated.

Table 1

Model Prediction of Phase Equilibria for Dolomite (NBS SRM 88a) at 1800 KA. Input Elemental Composition-Calcined (mole %)

Ca (49.23), Mg (48.47), Si (1.83), Al (0.34), K (0.24), Na (0.02),
Fe (0.32)

B. Predicted Phase Distribution of Component Oxides (mole %)

	CaO	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	Na ₂ O	Fe ₂ O ₃
Solid phase	48.7	48.4	--	1.39	--	--	--
Liquid phase	0.56	0.082	0.17	0.44	0.11	2.6x10 ⁻⁴	0.16

C. Predicted Phases (mole %)

MgO(s) (49.87), CaO(s) (48.71), 3CaO·MgO·2SiO₂(s) (0.73) Liquid (0.63),
Gas (0.06)

D. Predicted Major Liquids (mole fraction)

KCaAlSi₂O₇ 0.342, MgO 0.134, CaFe₂O₄ 0.170, CaO 0.108, Ca₂Fe₂O₅
0.082, CaAl₂O₄ 0.069, Ca₂Al₂SiO₇ 0.028, FeO 0.024, KAIO₂ 0.021,
CaSiO₃ 0.017

E. Predicted Alkali Liquid Components (mole fraction)

KCaAlSi₂O₇ 3.42 x 10⁻¹, KAIO₂ 2.14 x 10⁻², Na₂SiO₃ 3.67 x 10⁻⁴,
NaAlSiO₄ 1.20 x 10⁻⁴

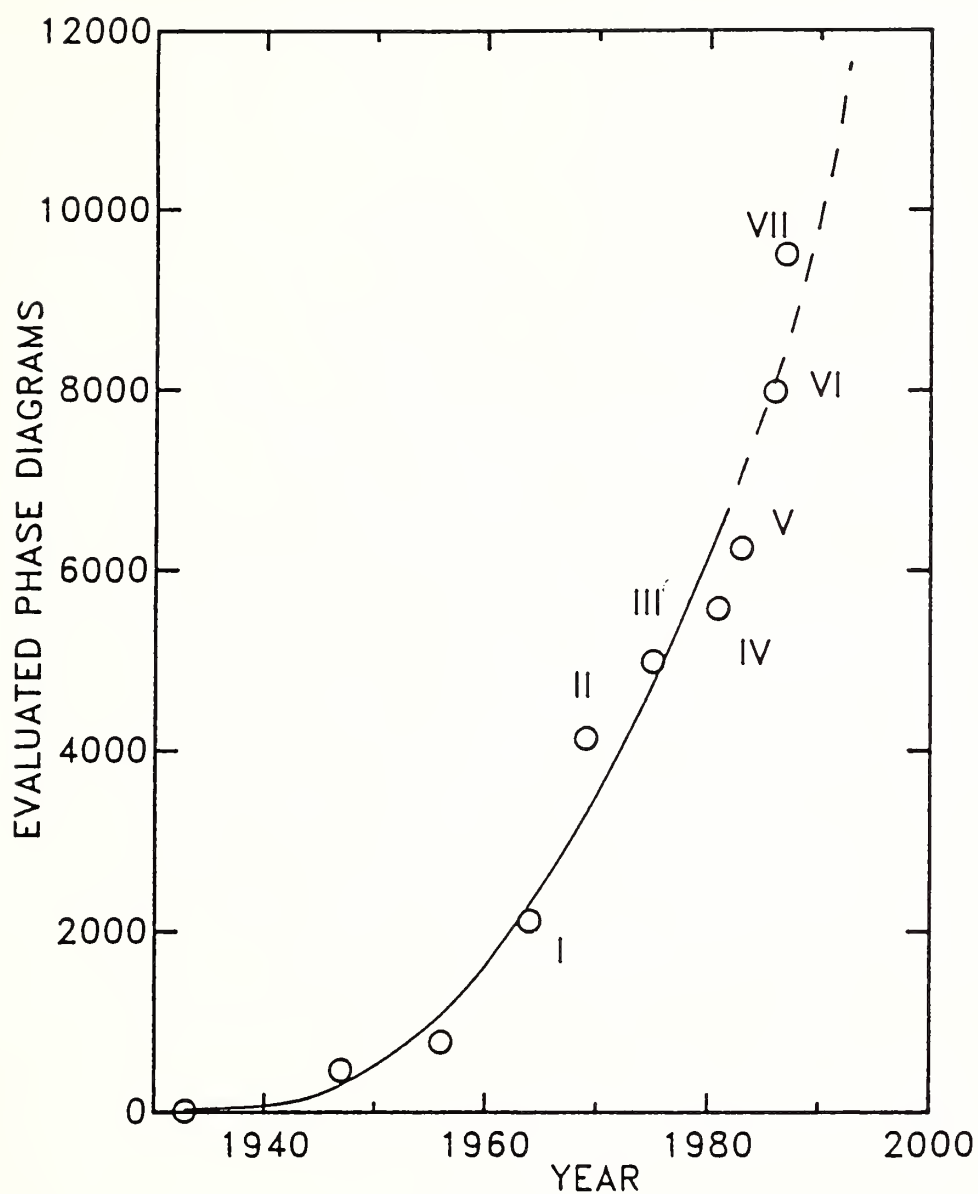


Figure 1. History of NBS-ACerS ceramic phase diagram compilation/evaluation cooperative activity, showing the cumulative number of diagrams and dates of each publication; the symbols I-VII refer to the PDFC volumes (VI and VII in preparation).

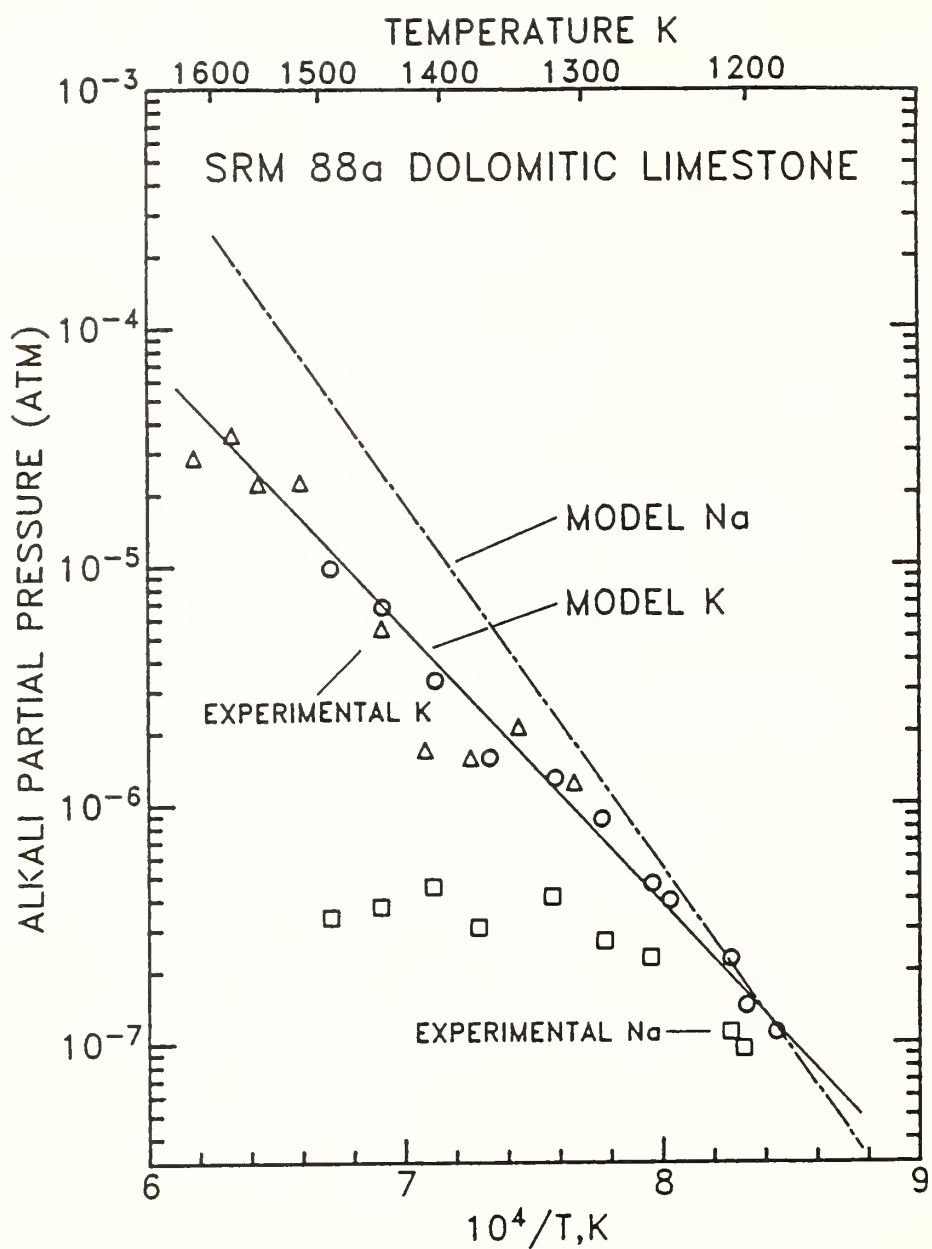


Figure 2. Comparison of model and experimental alkali partial pressure data for dolomitic limestone, showing good agreement between model and experiment and between the two independent measurement techniques of transpiration (triangular points) and Knudsen effusion (circle and square points) mass spectrometry. The solid and broken curves represent the model predictions of the K and Na pressures, respectively.

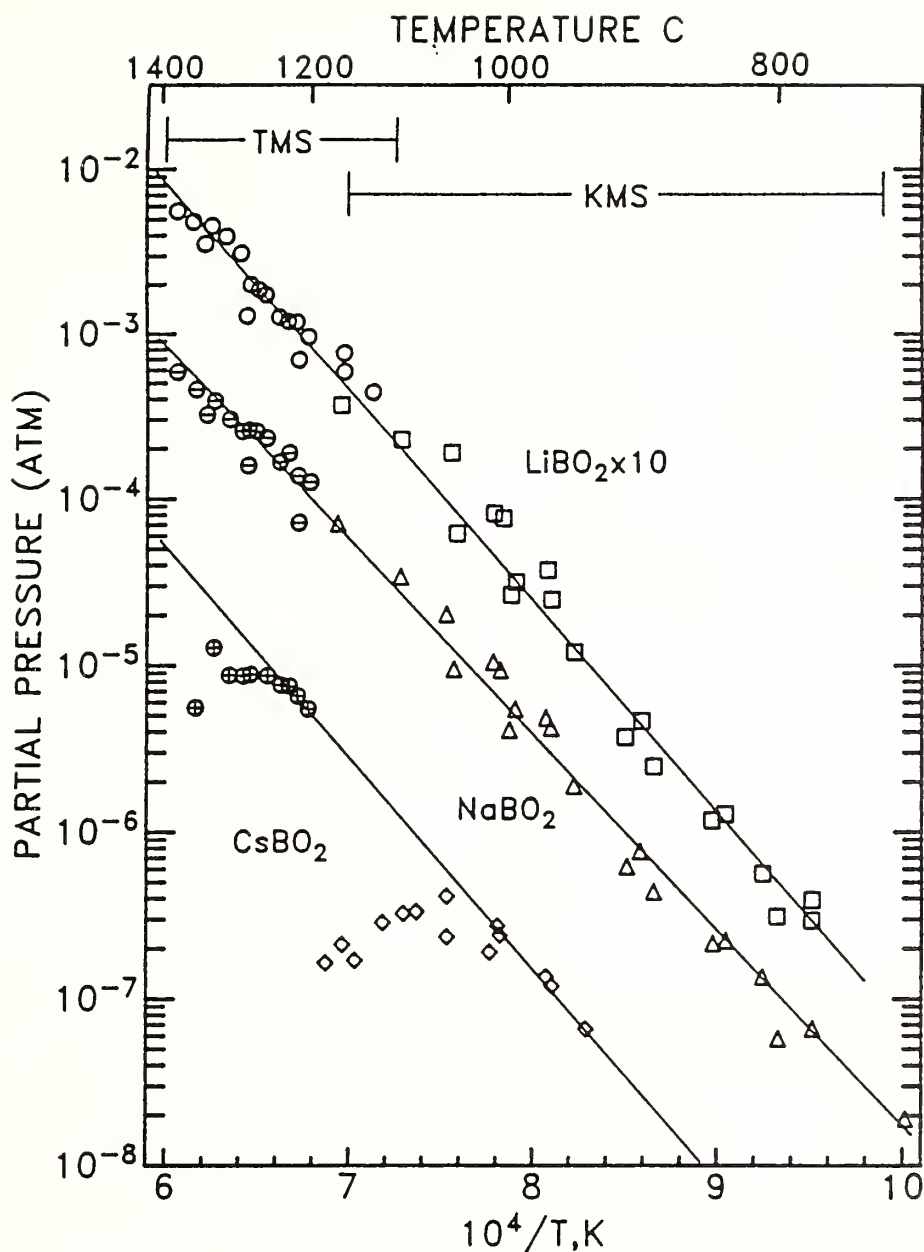


Figure 3. Partial pressures of metaborate species over a simulated nuclear waste glass, showing significant vapor transport of radionuclide (Cs) and host glass (Li, Na, B) components under processing conditions ($\sim 1150^\circ\text{C}$). The temperature intervals labelled TMS and KMS represent the regions for which transpiration and Knudsen effusion mass spectrometry data were obtained, respectively.

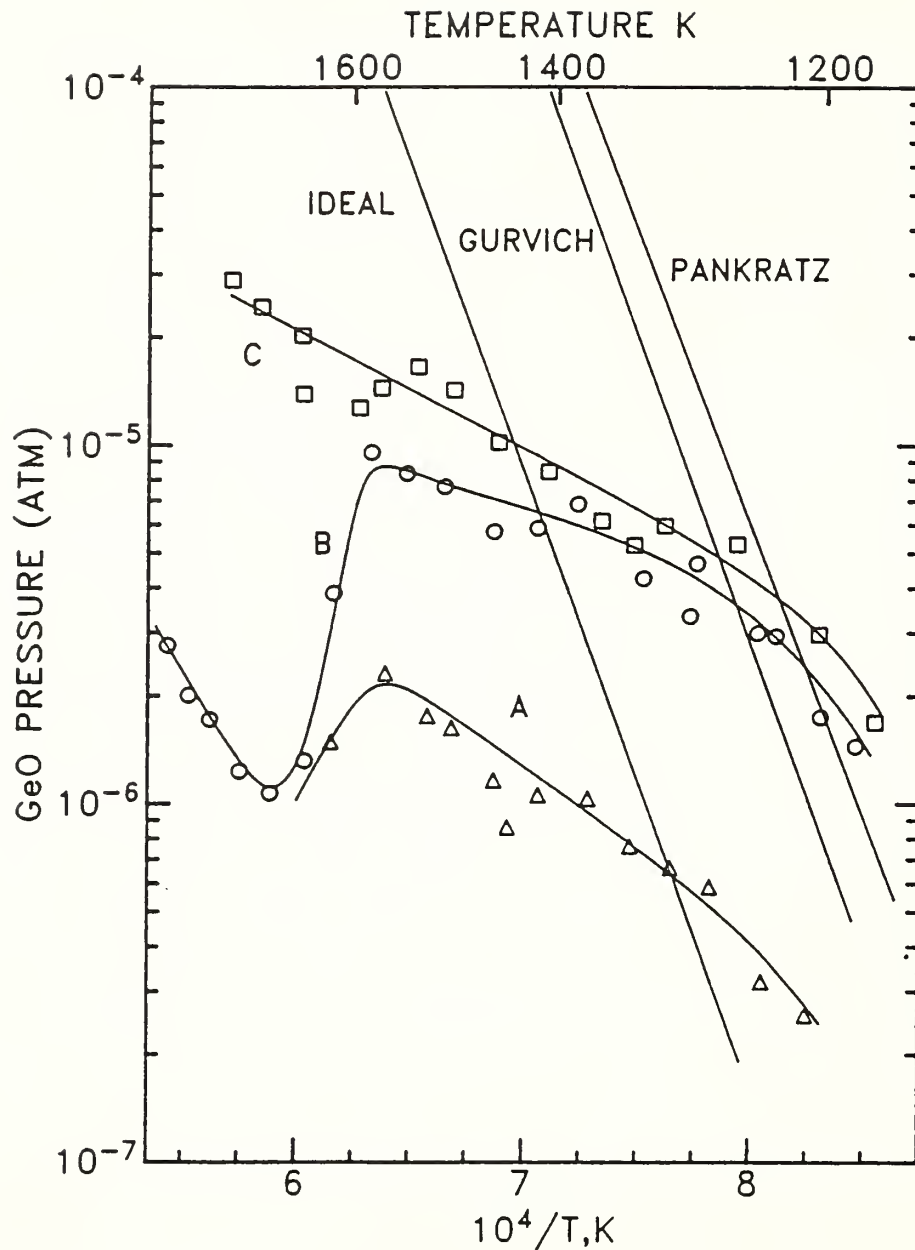


Figure 4. Partial pressures of GeO over $\text{GeO}_2\text{-SiO}_2$ glass samples, showing non-ideal mixing and nonequilibrium behavior. Comparison literature curves of Gurvich and Pankratz are for pure $\text{GeO}_2(\ell)$ and $\text{GeO}_2(\text{vitreous})$, respectively. Curve labelled IDEAL is based on an ideal solution with 5.8 mole % GeO_2 . Experimental curves A-C represent conditions of increased sample to orifice area and compositions of 13.3, 13.3, and 5.8 mole % GeO_2 , respectively.

3.3 MECHANICAL PROPERTIES OF CERAMICS

Ceramic materials are used where special properties, such as chemical resistance to corrosive environments, mechanical resistance to erosion and wear, and mechanical and chemical resistance to temperature extremes, are required. In commercial applications they are used as substrates for electronic packaging, containers for nuclear waste disposal, linings for geothermal wells, components for high-temperature gas turbines and heat exchangers, thread guides and wear surfaces for the manufacture of paper and clothing, cutting tools and cutoff wheels for the shaping and finishing operations used in the manufacture of various machines and tools, and insulating linings for reactors and furnaces in the coal-conversion and petrochemical industries. In defense applications, these materials are used as radomes, missile nose cones, turbine components in portable electric-generating facilities, electronic guidance systems and bearing surfaces in gyroscopes. Because they are brittle, ceramics are usually over-designed mechanically to avoid fracture during use. Investigations of fracture and deformation properties of these materials are needed to overcome technical difficulties associated with their brittle behavior, so that ceramics can be used in a wider range of applications.

Our program on ceramics has as its objectives: (1) the generation of new theories and data to elucidate fracture and deformation mechanisms in nonmetallic inorganic materials, (2) the development of new techniques for studying the fracture and deformation properties of these materials, (3) the collection of engineering data for structural applications, (4) the investigation of processes that result in strength degradation and wear, and (5) the investigation of ceramic microstructure and its relationship to mechanical behavior. Experimental techniques developed by the Mechanical Properties Group permit measurements of the mechanical properties of ceramics over a wide range of conditions: in vacuum at temperatures to 2973 K and in corrosive environments at temperatures that range from room temperature to 1873 K. This range of experimental capabilities is unique.

FY 83 Significant Accomplishments:

- o The molecular model for chemically enhanced crack growth established for vitreous silica has been extended to alkali ion containing glasses. The crack growth curves for the alkali glasses are more complex due to effects of ion exchange. The crack growth data for these glasses are being interpreted in terms of a pseudo-continuum model of discrete bond rupture: In this way, data from crack growth studies can be discussed in terms of the atomic forces that hold solids together.
- o Reliability maps have been developed for a commercial grade of pressureless sintered alpha silicon carbide. These maps characterize the high temperature strength of solids and the evolution of strength with time. By varying both the temperature and applied stress, three regimes of material response were observed for the alpha silicon carbide. These regimes correspond to (1) early failures from "crack growth", (2) strengthening at intermediate times from crack "blunting" or "healing" and (3) long-term failures (from general creep cavitation).

- o Through the use of controlled indentation flaws, it has been shown that times to failure for alumina under a fixed load can be accurately predicted from dynamic fatigue experiments. The type of flaw that causes failure, (machining flaw, processing flaw, etc.) has a major influence on the lifetime of the structure. The stress state of the flaw must be known in order to make accurate lifetime predictions.
- o Indentation fracture experiments were used to show that the toughness-temperature relationship in barium titanate represents an intrinsic crack-microstructure interaction. It was also shown that internal stresses generated by phase transformations can significantly affect the strength of barium titanate and other ferroelectric materials, especially when the flaw size approaches the grain size of the material. Dynamic fatigue tests were used to determine the stress corrosion susceptibility of this material.
- o Experiments in which hardness is measured as a function of loading rate and time at load show that the incidence of cracking in the vicinity of the indenter depends on the load, loading rate, time and on the content of water in the environment. Cracking can occur well after completion of the contact cycle due to the presence of residual driving forces about hardness impressions. From these observations it was deduced that there is a critical "incubation" time needed to develop crack nuclei within the deformation zone. These results have important implications with regard to extrapolation of strength data and the use of conventional tests for assuring component reliability.
- o Generally the characterization of materials by small angle neutron scattering has been conducted by diffraction techniques which provide size information in the range, 2 to 200 nm. Research in the past year has explored multiple neutron refraction as a technique of material characterization. The technique provides size information on scattering centers that are about one micrometer in size. These techniques have been used to monitor the porosity of ceramic compacts during sintering.
- o A theory has been formulated for the general time-dependent failure of brittle cracks that originate from residual stress concentrations. Theoretical relationships between failure stress and lifetime have the same functional dependence as residual, stress-free flaws, thereby indicating the importance of understanding the exact nature of strength-determining flaws. The theory provides a sound framework for the use of indentation cracks as a model defect system for materials evaluation.

Fundamentals of Fracture

Subtask 1

E. R. Fuller, Jr., T.-J. Chuang, R. F. Cook¹, S. W. Freiman, D. C. Greenspan², D. Kravitz, B. R. Lawn, G. S. White, and S. M. Wiederhorn

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Predictions of crack growth and fracture behavior, and hence, of component reliability can only be attained through a fundamental understanding of crack-tip structure and processes. In this subtask, studies are being conducted on basic fracture and deformation processes in ceramic materials and theories are being developed to understand these processes at a fundamental level. During the past year, work on this subtask included the development of an understanding of mechanisms of subcritical crack growth in glass and other ceramic materials. Glass was selected as a material for study because of its practical value and because it serves as a model for other brittle ceramics that are susceptible to subcritical crack growth. In addition to the work on glass, crack growth studies were conducted on model crystalline materials and on concrete mortar. These materials permit investigation of the effect of microstructure on strength and crack growth.

Environmentally Enhanced Crack Growth

A molecular model for environmentally enhanced subcritical crack growth in SiO_2 has been established. During the past year, work has been performed to determine if this model can be extended to alkali containing glasses such as soda-lime silica glass and a 33% Na_2O -67% SiO_2 glass. Crack growth data indicates that environments that enhanced crack growth in SiO_2 also enhance crack growth in alkali containing glasses. However, the crack growth curves for these glasses are more complex than those for SiO_2 . In H_2O , ion exchange appears to play a part in determining the $V\text{-}K_I$ behavior. Infrared reflection spectroscopy data established the strong effect of crack growth enhancing agents such as hydrazine, formamide and water on the corrosion behavior of the 33% Na_2O glass. Data is currently being taken on quartz in order to determine effects of vitreous/crystalline long range bonding on crack growth.

Work has also been continued to better understand electrostatic interactions between solid and environments that control crack growth in water-free environments. Data taken on vitreous SiO_2 indicate a similar dependence of the slope of the $V\text{-}K_I$ curve on the dielectric constant of the fluid to that observed for soda-lime silica glass. Work is continuing on this subject to obtain data using other, more accurate crack growth techniques, that are currently being developed for this purpose.

Atomistic Aspects of Crack Growth

The desire for understanding of fracture processes at a fundamental level has provided considerable impetus for atomistic modelling of cracks and crack-tip processes. Previous research has developed general techniques, using a defect Green's function approach, to study the discrete nature of bond rupture events in a brittle crystalline lattice. Using the understanding developed from this formalism, a quasi-continuum fracture mechanics model has been developed and the results applied to characterize environmental crack growth in various glass-environment systems. An important observation for vitreous silica is the insensitivity of the crack growth susceptibility to the type of stress corrosion environment, suggesting a double-kink nucleation mechanism as the primary fracture step. A Green's function formulation has been developed to describe this process.

Fatigue of Brittle Flaws Originating from Residual Stress Concentrations

A theory is formulated for the general fatigue response of brittle flaws which experience residual stress concentrations. The indentation crack is taken as a model flaw system for the purpose of setting up the basic fracture mechanics equations, but the essential results are expected to have a wider range of applicability in the strength characterization of ceramics. A differential equation is first set up by combining an appropriate stress intensity factor relationship for either point-contact or line-contact flaws with a power-law crack growth law. Analytical solutions are then obtained for the case of static fatigue. The resulting relation between lifetime and failure stress is shown to have exactly the same power-law form as the conventional solution for Griffith (residual-stress free) flaws. This "equivalence" is used as a basis for extending the results to dynamic fatigue. Comparison of these analytical solutions with their numerical counterparts defines the limits of accuracy of the assumed equivalence.

While the form of the lifetime relation remains invariant, the values of the crack growth exponent and coefficient differ significantly for flaws with and without residual stress. Accordingly, the application of conventional fatigue theory to evaluate crack velocity parameters, without due regard for the nature of the critical flaw, can lead to serious errors. Explicit conversion formulas are derived for transforming "apparent" velocity parameters for indentation flaws directly into "true" parameters. Since indentation flaws can be considered as a model crack system, these relationships provide a basis for the use of indentation techniques for materials evaluation.

Diffusive Mechanisms of High Temperature Crack Growth

Research has continued on diffusive mechanisms of cavity growth along grain interfaces at elevated temperature. Attention has been focused on the thermodynamic nature of crack growth in the high velocity region where elastic accommodation in the grains surrounding the crack is important. It is found that the crack driving force is related to the entropy production rate when the body is undergoing irreversible creep processes; further, by employing the finite deformation elasticity theory it is established that the driving force is identical to the well-known J-contour integral defined in the conventional fracture mechanics theory. The physical interpretation of the results can be summarized by the following statement: during the creep fracture processes, the energy input from the work done by the applied sustained loads, goes partially to the increase in the strain energy of the body and partially to the generation of heat in the body; this heat must be lost to the surrounding environment in order to maintain uniform temperature throughout the body.

Fracture Process Zones in Concrete Mortar

Cracking mechanisms in concrete and mortar have been the subject of research interest for many years now, particularly with recent developments in the theories of fracture for brittle materials. Relatively few studies, however, have been attempted to elucidate microstructural details of fracture zones that develop around propagating cracks in these materials. This lack of information has hindered the development of more realistic fracture mechanics theories based on micromechanisms of cracking. This collaborative research (with researchers from the Center for Building Technology, the University of

Virginia and the Inorganic Materials Division) explores the use of a fluorescent thin section technique for observing microstructural details of fracture zones around propagating cracks. Concrete mortar was used to illustrate the technique. Cracks were propagated in wedge-loaded double-cantilever beam specimens that were loaded both monotonically and cyclically; the specimens were then impregnated with an epoxy containing fluorescent dye and sectioned. Crack widths of two to three micrometers were easily discerned. Preliminary observations indicate tortuous crack paths with some branching, but very little microcracking not directly connected with a main crack branch.

New Approaches to Fracture and Deformation

Subtask 2

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The techniques of fracture mechanics have provided engineers with new and powerful techniques to evaluate the mechanical behavior of materials and to estimate the total allowable lifetime when a structural material is subject to mechanical forces. When the mechanism of failure is well understood, fracture mechanics techniques may be used directly to obtain a prediction of lifetime. When the mechanism of failure is not well understood, fracture mechanics in combination with probability theory is needed to develop a framework for structural design. In either case, it is important to be able to characterize the flaw size and the rate at which flaws grow in ceramic materials. A major portion of the work on this subtask during the past year was directed towards achieving this goal. This subtask is divided into three parts: (1) Methods of non-destructive evaluation; (2) Methods to characterize fracture toughness and crack growth; (3) Methods of predicting structural reliability.

Optical NDE: Light Scattering

Of the non-destructive evaluation techniques currently being considered to improve structural reliability, optical techniques have the advantage of speed, cleanliness and remote application to structural components. For more universal application of this technique a more detailed interpretation of the scattered signal is needed to distinguish and to characterize the types of scattering centers that are present in surfaces of materials. The relevance of these scattering centers to strength limiting flaws in materials must also be established. To this end, light scattering measurements have been made upon grooves with trapezoidal cross-sections in order to determine if the observed scattering could be described by a simple Fraunhofer calculation and to compare the observed scattering with that from grooves of less complex cross-section (shallow rectangular and V-shaped).

The simple Fraunhofer approach which worked well for describing scattering from the shallow rectangular groove has not been amenable to expansion to the trapezoidal case. The calculated scattering has consistently been more complex than the observed scattering, although the envelope of the calculated scattering has approximated what is observed. It appears that the model used

is too local to provide realistic scattering. This certainly would be expected for the two narrow grooves which should be in the resonance domain. The vector theory of Maystre, developed for the resonance domain, describes the observed scattering much more closely although discrepancies remain. As shown last year in the work with the V-shaped grooves, most of the discrepancy can be attributed to variations in the precise shape of the trapezoid cross section over the region of illumination.

Distributed Damage Evaluation by Small Angle Neutron Scattering Technique

Small angle neutron scattering, SANS, in condensed matter is a non-destructive technique that can be used to measure defects that are approximately 2 to 100 nm in size. Defects in high-strength, structural ceramics are generally sub micron in size, and consequently are difficult to detect until they have reached an advanced stage of growth which often leads to failure of the material. Small angle neutron scattering is a method of studying the evolution of these defects well before they have reached an advanced stage of growth. During the past year, transmission electron microscopy (TEM) and small angle neutron scattering (SANS) have been used to investigate two grades of commercial nonoxide structural ceramics. In one material, a magnesia-doped, hot-pressed silicon nitride, the defect source of the neutron scattering was found to be Fe and W inclusions in the solid. In the other material, a commercial grade of sintered α -SiC, microcracks and/or pores were responsible for the scattering. Small angle neutron scattering measurements were collected for scattering vectors in the range of $0.005 < Q < 0.17$, at three wavelengths, 5.45, 7.6, and 9.0 Å. The results suggest an average radius of the inclusions in hot pressed Si_3N_4 of 11 to 14 nm. The neutron intensity in the small Q region is sensitive to the longer dimensions of the neutron scattering source. In particular, scattering by large pores can be measured in ceramic materials. Both TEM and SANS data show no evidence of large pores in the hot pressed Si_3N_4 material. Data has been collected for two samples of α -SiC. One was tested as received; the other was exposed in air to 1370 °C for 3500 hours. Initial results indicate microcrack healing in the treated sample, however, the analysis is still in progress.

Porosity Studies by SANS Techniques

The elimination of porosity is a critical step in the densification process of sintered ceramic materials. A quantitative small angle neutron scattering (SANS) study is in progress to determine the average pore size in a green compact and a sintered body of pure YCrO_3 , both of which were isobarically pressed at 30,000 kbar and room temperature. The density of the green state compact material was 55% of theoretical density, whereas the sintered material was 93% of theoretical density. Taken at five wavelengths, 5.45, 6.25, 7.0, 8.0 and 9.0 Å, the SANS measurements revealed striking differences between the two samples. In particular, a strong wavelength dependence can be seen in the data for green state compacts. The behavior was characteristic of multiple refraction from large particles or voids and is consistent with the porous microstructure of the green state compact material. The sintered material shows no wavelength dependency indicating the pores or voids had grown to a size that was beyond the detection limits of the instrument. Although the qualitative aspects of the data clearly demonstrate the strong effect of ceramic processing on the population of neutron scatterers in these materials,

quantitative measurements of the void size are less straight forward. Therefore, a generalized theoretical technique is being developed to provide a quantitative analysis of the SANS data for densified ceramics.

Chevron Notch Testing

Because of the simplicity of loading under extreme environments, reproducibility of results and the small quantity of material required for each test specimen, the chevron notch bend test has been suggested for obtaining critical fracture toughness data on brittle materials. To evaluate this technique tests were performed on small specimens of soda-lime silica glass and silica glass in both wet and dry environments. It was found that the presence of a chevron notch did not insure the initiation of stable cracks. In some cases, considerable overloading occurred prior to failure, leading to significant overestimates of K_{IC} . The measured values of K_{IC} were also sensitive to moisture in the environment as a consequence of subcritical crack growth. The results of this study suggests that caution must be exercised when the chevron notch test is used on ceramic materials.

Reliability Maps

Reliability maps provide an alternative method to the pure fracture mechanics approach for lifetime prediction. Although the approach is probabilistic in nature, concepts of fracture mechanics can be factored into the method. Probabilistic concepts of strength are used for the construction of reliability maps which relate strength, failure time, and failure probability on a single diagram. These maps provide a general picture of the failure probability and can be used to establish engineering loads, and temperatures that are consistent with engineering requirements. Maps of this sort were obtained for magnesia-doped, hot-pressed silicon nitride (NC 132) and for yttria-doped, hot-pressed silicon nitride (NCX 34). A comparison of the two maps shows that the properties of NCX 34 are far superior to those of NC 132. For a given load, the NCX 34 is capable of operating at a higher temperature (~ 100 °C) than the NC 132, without long term loss in strength. Microstructural investigations suggest that creep cavitation at 1200 °C is not a serious problem in NCX 34, whereas it is for the NC 132. At 1300 °C, however, creep-cavitation also occurs in NCX 34, thereby weakening the test specimens. Studies are underway, to evaluate the effect of temperature and strength on the microstructure of these ceramics.

During the past year a pressureless sintered alpha silicon carbide (Hexoloy SA) was selected as the material for the development of new strength degradation maps because of its intended use as components for heat engines in the automotive industry. Maps were developed for this material at temperatures of 1200, 1250, and 1300 °C and at stresses of 200 MPa, 225 MPa, and 175 MPa. The objective of this study was to determine the role of temperature and applied stress on component strength. Although the work on this project is still continuing, important results have already been obtained relating the crack growth threshold to the temperature and the applied load.

Ultrasonic Marking of Propagating Cracks

Recent investigations at NBS have demonstrated the necessity of eliminating the influence of water when studying the effect of other environments on crack

growth. Because of the ubiquitous presence of water in almost all environments, this is most easily accomplished in crack growth studies by extending measurements to high ($> 10^{-4}$ m/s) crack velocities, at which water cannot diffuse sufficiently rapidly to reach the crack tip. During the past year a capability was developed to mark a propagating crack ultrasonically so that high-velocity crack growth measurements can be made on vitreous materials. The technique modulates the motion of a moving crack by superimposing an ultrasonic stress field on the "static" or quasi-static, fracture mechanics stress field of the crack. The resulting fracture surface has undulations that are equally spaced in time, corresponding to the period of the ultrasonic wave.

The technique has been used in several studies. In one, crack growth rates were measured for soda-lime silica glass in heptane over the velocity range of 10^{-7} to 10^2 m/s. These results were used to analyze proof testing data for this material-environment system and to critically evaluate proof testing concepts. In another study, the technique was used to monitor the growth of indentation cracks that grew to failure in strength tests. Since indentation cracks are similar to strength-determining flaws in brittle materials, these experiments shed considerable light on the failure process in these materials. The technique is currently being used to characterize the high-velocity region ("Region III") of glass in various environments. These results will elucidate the role of dielectric shielding in the elementary fracture process.

Engineering Evaluation of Ceramics

Subtask 3

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Extensive studies are being conducted on the strength of ceramic materials intended for use in a variety of commercial and military applications. Materials being studied include: geothermal cements used to line wells that tap hot water reservoirs deep within the earth; refractories intended for use at elevated temperatures in slagging gasifiers; partially stabilized zirconia linings for adiabatic diesel engines; nonoxide ceramics for heat engines; titanate ceramics for capacitors; and ceramic materials for electronic chip carriers. Work on this subtask is often conducted at the specific request of other government agencies.

Corrosion of Refractories by Slag Penetration

This project deals with the structural integrity of refractories that have been penetrated by coal slag. As the temperature is increased, slag penetration is expected to have an adverse effect on the creep behavior of refractories by modifying the viscosity and thickness of glass at grain boundaries. Increasing the thickness of the slag at grain boundaries or reducing its viscosity increases the creep rate and activates strength degradation processes that are associated with creep. Hence, we are concerned with the effect of vitreous phases on the rheology and mode of strength

degradation of refractories. Creep and creep-rupture of commercial grades of aluminum oxide are being measured as a function of glass content, glass composition, load and temperature. Creep measurements are also being made on a $\text{ZrO}_2 \cdot 2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ refractory which contains a substantial glass bonding phase. This refractory is intended to simulate the mechanical behavior of refractories that have been completely penetrated by slag. Although initial studies are being conducted in four-point flexure, tensile and compressive creep measurements will also be made on this material to compare the three measurement techniques. Work on this project is an extension of earlier studies of creep of refractories, and is expected to continue for the next 3 years.

High-Temperature Crack Growth and Fracture of Structural Ceramics

Because of national goals for self sufficiency in energy and for substitution of critical materials, ceramics are increasingly being considered for high-temperature, structural applications. An important element needed to assess their reliability under severe conditions is in the development of an understanding of their crack growth and fracture behavior. To address these issues, research is being conducted to characterize the crack growth and fracture behavior of advanced high-temperature ceramics.

Research in the past year has concentrated on the crack growth behavior of a pressureless sintered alpha silicon carbide (Hexoloy SA) at 1500 °C. The double torsion fracture mechanics configuration was used to collect data. Because specimens fractured catastrophically, initial studies, using a constant displacement rate technique, suggested the absence of subcritical crack growth. However, upon closer inspection, regions of intergranular, subcritical extension were observed between the transgranular fast-fracture regions. Currently, crack growth rates are being measured by static load tests (constant stress intensity factor). Thus far, only transient behavior has been observed, cracks gradually decelerating and eventually stopping at a given applied stress-intensity-factor.

High-Temperature Fracture in Reactive Environments

Materials used in the elevated temperature regions of fossil-fuel fired systems are subjected to the aggressive environments that are produced by combustion processes. These aggressive environments can adversely influence the structural integrity of the material. In fact, when a component constructed from these materials is subjected to an applied stress, the environment and stress can act synergistically to degrade the strength of the component. Because of the numerous structural applications for ceramics in high-temperature regions of coal conversion systems (e.g., heat exchanger and gas-fired turbine components), an understanding of the critical factors that determine the thermochemical/mechanical integrity of these ceramic materials is essential.

To address these issues, a facility has been constructed at NBS for the fracture testing of structural ceramics at elevated temperatures and at one atmosphere pressure in controlled gaseous environments. The system consists of an enclosed electric furnace, capable of temperatures up to 1600 °C, which is installed on a universal testing machine. The gaseous test environment is supplied to the furnace by mixing gases from pressurized gas cylinders; a

steam generator is used to supply the appropriate partial pressure of water vapor. Using this facility, fracture toughness tests were conducted on chevron-notched, four-point flexural specimens. Three grades of silicon carbide used in these studies were tested in air, and in an environment of nitrogen, oxygen, steam, carbon dioxide and sulfur dioxide. Only a slight influence of either loading rate or environment on fracture toughness was observed for a sintered alpha silicon carbide and for a grade of reaction sintered silicon carbide material containing a bimodal distribution of grain sizes. In contrast, a second grade of reaction sintered silicon carbide material, which can be characterized by its fine grain structure, showed a strong sensitivity of fracture toughness to loading rate. The high values of fracture toughness obtained on the fine grade material at the low loading rates are indicative of creep blunting and viscous fracture.

Polymer Concrete for Geothermal Applications

Because of their greater resistance to abrasion and corrosion, and their greater strength per density, concretes have a number of advantages over metallic materials in geothermal systems. Offsetting these advantages are the poor impact resistance, low fracture toughness, and a sensitivity to thermal shock and subcritical crack growth. In order to design effectively with these materials and to utilize them in geothermal systems, fracture properties have to be measured and damage mechanisms assessed under conditions that simulate exposure to geothermal environments. This year, the fracture toughness of two polymer concrete materials was evaluated using several fracture mechanics configurations. By varying the test configuration it was possible to elucidate the interaction of cracks with the microstructure of these materials. The extent of stable crack growth in specimens of different geometry correlated with the measured toughness, and hence, supported the concept of a rising crack-growth resistance curve for these materials. This work will be published as part of the ASTM Symposium on Chevron-Notched Specimens: Testing and Analysis, held in Louisville, KY, April 21, 1983.

Durability of Geothermal Well Cements

The durability of cement specimens has been evaluated after exposure to geothermal fluids in a well in the Cerro Prieto geothermal field in Mexico. This well was operated by the Comision Federal de Electricidad of Mexico, who also assisted in the exposure tests. Sixteen potential compositions for cementing operations in geothermal wells were selected for these durability tests. Specimens were exposed in the well and in special vessels above ground near the wellhead. Following periods of exposure of one day, three months, six months, and one year at $\sim 200^\circ\text{C}$ the compressive strength and water permeability of the specimens were measured. Precured cubes of the cements that were used in the tests showed considerable erosion with exposure to the geothermal fluids. The compressive strength of these specimens decreased with exposure time whereas their permeability increased with exposure time. In contrast, a set of protected sandstone-molded cement specimens fared better, their properties generally improving with time. This second type of specimen was exposed under conditions that are more representative of the conditions a cement would experience as a well liner. Properties of the cements were evaluated in cooperation with the Instituto de Investigaciones Electricas, Cuernavaca, Mexico.

Ceramics for Diesel Engines

Recent research supported by the U.S. Army and the Department of Energy at the Cummins Corporation demonstrated the practical value of adiabatic diesel engines as a means of improving the thermal efficiency of these engines. A 10 percent improvement in diesel oil consumption was registered recently by the Cummins Corporation in a standard diesel engine, which had been converted into an adiabatic engine. The conversion was achieved by coating all parts of the engine contacting hot gases with zirconium oxide. Improved efficiency (up to 50 percent) is anticipated with the use of either thicker zirconia coatings, or partially stabilized zirconia inserts in the cylinder wall liners. The Department of Energy, cosponsor of this research program, has requested support from NBS to evaluate the microstructure and the mechanical properties of ceramic materials currently being used in the diesel engine program. Components of partially stabilized zirconia from the adiabatic diesel engine developed by Cummins were obtained and examined by scanning transmission electron microscopy (STEM). Other billets of similar partially stabilized material were obtained from the manufacturer and are being prepared for thermal cycling experiments. This material undergoes phase transformation as a result of thermal and mechanical stress and the effect of the transformations on mechanical behavior must be understood to insure the structural integrity of diesel engines. The transformations will be monitored by STEM techniques and the results will be compared with materials obtained from diesel engines.

Fracture of Ferroelectric Ceramics

Ferroelectric ceramics, such as barium titanate and lead zircona titanate, which are used in transducers, capacitors, and power supplies, fracture from small processing and handling flaws. These materials are also susceptible to environmentally enhanced crack growth. During the past year controlled flaw tests were run on BaTiO_3 as a function of temperature and crack size/grain size ratio. A monotonic decrease in strength, corresponding to an $\sim 40\%$ decrease in K_{IC} , was observed as the temperature increased from room

temperature to the Curie temperature ($\sim 120^\circ\text{C}$). The strength then levelled off. The behavior was reversible with temperature, indicating intrinsic thermal effects on K_{IC} . It is suggested that crack/twin interactions can

account for the observed K_{IC} behavior. Deviations from indentation fracture models at crack sizes approaching that of the grain size were used to show that microstructural stresses arising during the cubic to tetragonal phase transformation can be important for failure from small flaws.

Dynamic fatigue tests were run in H_2O on indented BaTiO_3 . A crack growth exponent, $N = 67$, was calculated; this value is in the range of that determined on other ferroelectric ceramics.

Establishment of a Fracture Mechanics Data Base

Data on critical fracture toughness/fracture energy and subcritical crack growth parameters are necessary for design with glass and ceramics. Values of critical fracture toughness, fracture energy and crack growth exponents were compiled from published literature and from private sources for a wide variety of glasses, single crystals, and polycrystalline ceramics. A computerized data retrieval system was developed to allow the selection of data by

material, investigator, or experimental technique. Plotting routines allow K_C or γ to be plotted versus glass composition, ceramic grain size, elastic modulus, etc. The system has been used to demonstrate trends in fracture properties with the above variables.

Glass-Metal Seals

Glass ceramics are used in glass-to-metal seals because their thermal expansion coefficient can be adjusted to match that of the metal and because crystallization of the glass increases the strength of the seal. During the past year, work was performed on the effect of microstructure of a $\text{Li}_2\text{O-SiO}_2$ base glass ceramic on the critical fracture toughness and the susceptibility to subcritical crack growth. Microstructures corresponding to three different heat treatments were examined. Indentation procedures were used to obtain K_C and dynamic fatigue data. An effect of crystal size on K_C was observed; the glass ceramic containing the largest lithium-metasilicate crystallites yielded the highest fracture toughness. Although the dynamic fatigue tests are still in progress, preliminary results show only small differences in stress corrosion susceptibility between the three microstructures.

Failure of Ceramic Multilayer Capacitors

Electrical breakdown of ceramic capacitors can lead to the failure of important electronic components in computers used for telecommunication purposes or for military applications. It has been suggested that the failure of ceramic capacitors may be associated with cracks in the ceramic, which can lead to a short circuit between electrodes if subcritical crack growth occurs. This study consists of two parts: (1) the establishment of relationships between ceramic composition, fracture toughness and subcritical crack growth susceptibility of capacitors and (2) a determination of the effect of cracks on the current-voltage-time characteristics of capacitors in order to establish a minimum crack size as the cause of electrical failure. Indentation techniques are being used to introduce cracks of a known size into a capacitor. The crack size is either measured optically or is evaluated from the strength of the capacitor. To date, we have examined two capacitor compositions: BX (barium titanate) and NPO (neodymium titanate). We have shown that there is a strong interaction between cracks in the ceramic and the metal electrode layers, leading to fracture toughness values higher than would be measured on the ceramic alone. Electric fields were applied to the indented capacitors for several periods of time, however, no effect of electric field on crack length was observed. Leakage currents under an applied field of 100 V were monitored on capacitors with and without indentation induced cracks. In both cases the current required ~ 2 days to stabilize in the range of 10^{-13} amp. However, the capacitor containing the cracks reached a steady state value of current about a factor of seven times larger than that of the as-received capacitor. Current-time plots are being obtained for these capacitors under various conditions in an attempt to establish failure criteria. Effects of external environments, e.g. H_2O are also being studied.

Thermal Shock of Glass and Ceramic Spheres for Solid Thermal Carriers

As a result of concern over the effect of large thermal fluctuations upon the mechanical stability of small (0.1 mm to 1 mm) diameter spheres currently being considered for use as thermal carriers in solar collectors, "worst case" thermal shock experiments were conducted on spheres of glass or aluminum oxide. As currently planned, the spheres are to be dropped past an opening in the solar collector tower through which focussed sunlight will enter. The spheres will spend ~ 2 s in sunlight having a power density of $\sim 1 \text{ MW/m}^2$. The spheres are expected to reach temperatures of $\sim 1000^\circ\text{C}$. Because the spheres will be spinning as they fall through the sunlight, and because they will only partially absorb the sunlight, they are expected to heat uniformly in actual use. Since thermal stresses are higher when spheres are not heated uniformly, our initial experiments employed a CO_2 laser which was aimed at stationary spheres. This procedure provided a more severe test of the thermal shock capability of the ceramic spheres. Thus far, we have looked at the effects of laser power on spheres of soda-lime silica glass, alumina and ruby, and at the effects of cyclic illumination on alumina and ruby spheres. Although surface melting occurred for all specimens, no cracking was observed on initial exposure. However, when the alumina spheres were illuminated for 20 cycles, fine surface cracks were observed. Given identical treatment ruby spheres did not crack in this fashion. Tests to date suggest that fracture due to thermal shock will not be a problem in the solar collectors.

Contact Processes in Ceramics

Subtask 4

B. R. Lawn, A. C. Gonzalez, B. J. Hockey, H. Multhopp, D. E. Roberts, and S. M. Wiederhorn

Contact damage studies provide valuable information on fundamental deformation and fracture properties of materials and can be used as the basis for modelling important practical processes such as erosion, wear and the machining of ceramic materials. During the past year, our effort has been directed towards the development of a detailed understanding of the fracture and plastic deformation that occurs during contact. We currently have projects concerned with: (1) indentation damage; (2) dynamic hardness; (3) effect of sliding contact on strength.

Indentation Damage

It is now recognized that ceramics can be deformed irreversibly at room temperature. Moreover, this deformation plays a dominant role in the initiation and propagation of cracks that control the strength and wear behavior of ceramic materials. Recognizing this fact, a considerable effort has been made in the past few years by Dr. B. R. Lawn and his colleagues at the University of New South Wales to understand the micromechanics of contact damage in brittle materials. With the transfer of Dr. B. R. Lawn from the University of New South Wales to the National Bureau of Standards, this effort has also been transferred to NBS. During the past few years much progress has been made on the analysis of stress fields in elastic/plastic contact. The most important finding from these studies is the identification of the vital role of residual stresses in the associated fracture process. These stresses

have been largely ignored in the ceramics testing literature, as a result of which much of the published data relating to strength and erosion is in error.

One of the important applications of indentation analysis lies in the evaluation of basic fracture parameters. Indentation flaws of predetermined size can be placed in strength test pieces with great control, thereby allowing for accumulation of strength data with unprecedented experimental simplicity and specimen economy. This gives a powerful tool for measuring toughness and crack velocity parameters, without the need for statistical data manipulation. This aspect of the work is at a highly developed stage and has resulted in several publications in the last year or two.

A second application is the characterization of flaws. Because the location of the indentation flaw, as well as the size, can be predetermined, one can follow the flaw evolution to failure throughout the entire strength test. This is a unique feature of strength analysis. Studies of this kind have now established that many (probably most) of the strength-controlling "natural" flaws in ceramics respond in an analogous manner to the indentation cracks, particularly as regards the influence of residual stresses. Flaws introduced by particle impact, abrasion and machining certainly fall into this category. Direct microscopic and acoustic emission techniques are being used to monitor the indentation process in a number of brittle materials.

Dynamic Hardness

Because of the importance of hardness to the nucleation of cracks during short term contact events in erosion and machining, an attempt is being made to measure the dynamic hardness of ceramic materials. The method uses an electrically driven hardness indenter and operates over several decades of time, 10^{-3} to 10^{-4} seconds, and delivers penetration loads between 0 and 10 Newtons. The technique is capable of developing several different wave forms for the penetration load: (1) sinusoidal, (2) triangle, (3) square, and (4) ramp. Current emphasis on equipment development is directed towards the addition of a means of sensing the displacement of the indenter as it penetrates into the sample. This is accomplished through the use of electronic transducers.

Experimental studies during the past year have been carried out on soda-lime silica glass, copper, and tungsten using sinusoidal impulse loads. As the period of impulse decreased from $\sim 10^4$ s to 10^{-2} s the hardness of these materials was found to increase by ~ 10 percent for copper and glass, and by ~ 20 percent for tungsten. A short note discussing this work has been published by the Journal of Materials Science. It is also observed that the duration of load has significant influence on the threshold for crack formation in glass. During the coming year the effect of load duration on fracture will be studied extensively.

Effect of Sliding Contact on Strength

This area of work for the Division is intended to enhance understanding of contact damage in structural ceramics at elevated temperatures. The data obtained on this project will be used for the assessment of theoretical treatments of strength degradation caused by sliding contact stresses. Equipment has been constructed to measure the adhesive and frictional forces

that develop between ceramics at elevated temperatures. Tests have been conducted on glasses to determine the temperatures at which the friction is enhanced as a result of adhesion at the contact interface. Studies indicate that the coefficient of friction increases precipitously at a temperature of ~ 200 °C below the fictive temperature. Microscopic examination of the contact interface indicates a pronounced effect of temperature and load on the type of fracture damage that occurs as a result of contact.

The second part of this project is concerned with the influence of these frictional properties on the strength characteristics of the contacted surfaces. The frictional contact produces cracks, which reduce the strength. Extensive testing has been carried out on glass, investigating the effect of normal contact load, friction coefficient, and temperature, on strength. It is found that strength is in fact relatively insensitive to all these variables, contrary to the initial assumptions of design engineers. A detailed fracture mechanics model of the crack process describes the data well, and moreover establishes a sound basis for optimizing resistance to degradation (e.g., by selecting materials of high toughness). Work is continuing on other materials and on extending the experimental temperature range.

Microstructural Analysis

Subtask 5

N .J. Tighe, T.-J. Chuang, G. A. Danko, E. N. Farabaugh, and B. J. Hockey

The objective of this subtask is to evaluate the effect of microstructure on the mechanical properties of ceramics. Scanning and transmission electron microscopy are the principal techniques used. During the past year, work was directed at (1) the development of analytical microscopy techniques that can be used to assess the microstructure of ceramics, (2) the study of crack tip deformation to evaluate elastic-plastic theories of fracture, and (3) the analysis of structural ceramics that have been deformed at elevated temperatures to improve our understanding of high-temperature deformation and fracture processes.

Analytical Microscopy Techniques

The scanning transmission electron microscope (STEM) has analytical capabilities for imaging and chemical analysis. Images formed by electrons transmitted through a specimen in conventional or scanning mode are supplemented by images formed by back-scattered (BS) and secondary electrons (SE) from surface and sub-surface. By combining these techniques it has been possible to characterize cracks, inclusions and pores that intersect the surface as well as those that lie as deep as several micrometers below the surface. Chemical analysis using the energy dispersive spectroscopy (EDS) capability on the STEM can be influenced by sub-surface inclusions such as W and Y in the silicon nitride. By using the BS imaging mode which differentiates atomic number contrast, such interactions can be identified and clean areas selected for analysis. Stereo microscopy using BS images was used to show the spatial distribution of heavy inclusions.

Standards and standard measurement techniques are currently being developed for application to electron energy loss spectroscopy (EELS), which is used for light element analysis in engineering materials and in biological environments. Thin films containing elements such as N, O, Si, Al, Zr that were prepared by electron beam evaporation had to be less than ~ 10 nm in thickness in order to carry out meaningful calibration measurements. Data from these films are currently being used to calibrate EELS spectra from bacteria. Precipitates in natural bacteria and in bacteria doped with specific metal impurities were identified by the EELS technique with the objective of identifying the process by which these impurities are metabolized by the bacteria.

In collaboration with the Ceramic Science Group, the Arizona State University, computer program for calculating high resolution images was compiled for use in the NBS mainframe computer. This program will be used to develop further the image analysis capability of the STEM facility.

Crack Tip Deformation

Transmission electron microscopy has proven to be an extremely valuable technique in the study of crack tip structures and the various processes that can occur in the vicinity of crack tips. These studies are primarily aimed at providing an experimental basis for the various fracture models developed from theoretical considerations both at NBS and elsewhere.

Most recently, these efforts have been directed at determining the specific role of plastic deformation during fracture under conditions where plasticity is limited to the crack tip zone. These conditions are realized not only during the low temperature fracture of many so called semi-brittle ceramics and metals, but also in highly brittle materials at service temperatures above their brittle-to-ductile transition point. Initial studies on MgO have confirmed the occurrence of localized crack tip plasticity during controlled crack propagation. Detailed analysis have shown that the crack tip dislocation configurations produced critically depend upon the nature of the applied stress, and that they generally result from the activation of unresolved dislocation sources located near the tip of a moving crack, not from the actual crack tip as often presumed. Thus while crack tip plasticity can result in the formation of geometrically blunting type dislocations, these dislocations rarely intersect the actual crack front. Instead they generally intersect the crack interface at an angle to the crack front line or for arrested cracks tips are located ahead of the point of arrest. Excluding contributions to the macroscopic crack opening displacements that occur behind the crack tip, the primary effect of crack tip plasticity is to reduce the local stresses acting on the crack tip, which remains essentially atomically sharp. As such, the results fully support the dislocation shielding models of brittle fracture recently advanced at NBS by R. Thomson and his colleagues. The results of this study of crack tip plasticity in MgO were presented at the Annual Meeting of the American Ceramic Society and at a Symposium on "Deformation of Ceramics" held at Pennsylvania State University, the proceedings of which will be published.

Somewhat similar crack tip studies are planned to investigate not only the effect of plastic deformation but other stress relaxation processes on the fracture of more technologically important materials. These will include various semi-conductors, such as silicon, and a variety of advanced ceramics materials whose structure and properties are currently being investigated in other CMS programs. In these studies the effects of temperature and environment will be considered. To this end, a high temperature ball-on-ring test apparatus for controlled crack propagation studies on small samples (suitable for TEM examination after subsequent thinning) has been constructed.

Structural Ceramics

The scanning transmission electron microscope (STEM) was used to characterize microstructural changes that occurred due to static creep of silicon nitride and silicon carbide at elevated temperatures. Test specimens were examined after deformation to find direct evidence for specific failure mechanisms such as creep cavitation, microcrack healing, stress corrosion cracking and slow crack growth. Creep cavitation was observed in both yttria- and magnesia-doped, hot pressed silicon nitride. Although creep cavitation was responsible for the failure of both of these materials at elevated temperatures, the mechanisms of creep were material specific and were somewhat different for the yttria- and magnesia-doped materials. The STEM observations were correlated with results obtained by small angle neutron diffraction spectroscopy (SANS) on both the silicon nitride and silicon carbide samples. It was possible to identify the specific defects such as cracks, pores and inclusions that caused neutron scattering and absorption. The measurements on the yttria-doped, hot-pressed silicon nitride were used to obtain parameters that describe high temperature diffusional crack growth (discussed below).

Diffusional Crack Growth

The first TEM micrographs of diffusional cracks have been observed in silicon nitride doped with Y_2O_3 (NCX 34). Among other ceramic materials, only alumina has been reported to contain diffusional cracks (Chuang-Rice cavities). Hence, the observation of such cracks in a second ceramic material suggests that diffusional crack growth may be a common mode of failure in ceramics at elevated temperatures.

Under investigation was a four-point bend specimen tested under constant maximum applied stress of 350 MPa at 1300 °C. After 117 hours the bend specimen was deliberately fractured as part of the test program. Using high power transmission electron microscopy, several diffusional cracks with a clearly defined geometry were detected near the tensile surface of the specimen. From published data for physical constants, it was established that the observed crack tip velocity closely agrees with that predicted by a theory developed by T.-J. Chuang of the Inorganic Materials Division.

As a by-product to this study, the surface and grain-boundary diffusivities of Y_2O_3 in Si_3N_4 matrix were also deduced. The difficulty of obtaining accurate diffusion data on materials is well known by materials scientists. In experimental studies, several orders of variation in diffusivity are the norm. Thus, the creep test method may serve as a valuable alternative to standard test methods for obtaining meaningful diffusion data for materials. Additional studies are currently underway to test this possibility.

3.4 GLASS AND OPTICAL MATERIALS

The objectives of this task focus on the development of scientific concepts, measurement technology, scientific data base, standard reference materials, and materials characterization as they relate to the material glass and to optical materials. Because certain military and civilian uses of glass products are of specific interest to the Government, the NBS has a long-standing expertise in this field. This expertise is being used by government agencies and industrial producers and users of glass and accounts for a large number of technical requests from these groups as well as for a number of collaborative programs with other government agencies.

For the purpose of this report, the work of the Group has been divided into six subtasks. Subtask 1, the Physics and Chemistry of Glass, addresses such fundamental factors of glass formation as melt viscosity and devitrification. It also addresses principles such as nucleation and phase separation which govern the formation of recrystallized glasses, an important branch of glass technology which has resulted in new and improved materials.

The unique properties and distinct processing technology of glass have resulted in a well focused and organized industry which is represented in numerous standards organizations and technical and legal working associations. Through these organizations, the Glass Group obtains input from the industry for new standard reference needs. The priority list is continuously updated as technological, energy, raw material and legislative situations change. An ASTM-appointed NBS Research Associate as well as industrial representatives participate in this priority-setting process. SRMs under development reflect the needs of high-technology applications of glass (Glass Dielectric Constant SRM), changes in the energy utilization picture (Glass High Temperature Resistivity SRM) and the dominant role of glass viscosity in the shaping of glass by thermoplastic processes such as casting, drawing, pressing, blowing and slumping. SRM-activities of the Group which relate to Standard Reference Materials for Glass Processing and Use are discussed in Subtask 2.

Subtask 3, Glass Standard Reference Materials for Other Industries, deals with SRM relating to particular uses of glass (e.g., nuclear waste utilization) or to SRMs where the unique homogeneity, durability and/or ability of thermoplastic shaping of glass is being exploited.

Subtask 4 develops new processing technologies and measurement bases for such technologies. It involves products, such as fiber optics data and communication links, high energy lasers for nuclear fusion, integrated optics and prosthetic devices.

The thin film synthesis and analysis facility of the Group, designed to apply a novel co-evaporation technology to problems of integrated optics and low loss optical coatings, is also engaged in cooperative projects with other parts of the NBS. It has been used to study mechanical properties of films as well as to synthesize metal films for passivation and interface studies. These activities are described in Subtasks 5 and 6.

Collaborative work with universities, guest workers and Research Associates has been a source for stimulating scientific exchange as well as scientific manpower. One Group member received a Doctoral Thesis from Alfred University for work done at NBS. Another Doctoral Thesis (Stanford University) resulted from work for which a Group member was co-supervisor.

Several of the listed activities were joint programs with other agencies, universities and other parts of NBS. Outside financial support for research projects was received from: Lawrence Livermore National Laboratory for laser glass developments and consultations to the fuel-shell program; Kigre, Inc. for characterization of laser glasses as part of a program sponsored by the Office of Naval Research; Naval Research Laboratory for work on fluoride glass optical films; NBS Office of Standard Reference Materials for SRM developments; Department of Defense for development of small particle standards; Department of Energy for assistance in developing and procurement of nuclear waste leachability research materials; U.S. Post Office and the NBS Office for Nondestructive Evaluation for development of fluorescence standards; Office of Naval Research for research on fracture of ceramic films; Office of Naval Research for work on torpedo fuel; Department of Energy for work on the viscosity of coal slags.

FY 83 Significant Accomplishments:

- o A study of the heterogeneous nucleation behavior of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ glass has been concluded. The results showed that the effectiveness of platinum as a nucleating agent is not dependent on platinum concentration as reported in the literature. The results also showed that the nucleation behavior studied is well described by classical nucleation theory. This is in contrast to the case of homogeneous nucleation of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ which shows marked deviation from classical theory. Controlled crystallization of glass is used in the production of recrystallized glass ceramics and an understanding of nucleation is of importance for tailoring of product properties.
- o Melt viscosities of compositions in the diopside-anorthite system were determined and analyzed, and a manuscript was prepared. Data in the diopside-anorthite-albite ternary have been completed and are being analyzed. These data are of interest to the geologist and have implications for the structural understanding of silicate melts. They show, together with Raman-spectroscopic results, that anorthite has a three dimensional framework while diopside has a completely depolymerized structure. The data are also important

for the possible synthesis of low cost glasses having high chemical durability and good electric properties.

- o A Glass Dielectric Constant Standard Reference Material and Certificate were issued (#774). This SRM is of major interest to the electronic industry and to the industries producing dielectric materials. The SRM allows the checking of test methods and the calibration of equipment. While its major application is in electrical and electronic applications of glass, other industries, such as producers of high polymer dielectrics are expected to use this glass standard because of its superior aging characteristics.
- o A facility for improved measurement of high temperature electric resistivity of glass has been set up and is used to compare data with collaborating laboratories. Agreement between laboratories is now within 5 percent, compared with a previous discrepancy of 30 percent in the very high temperature region. These measurements standards are needed by the glass industry for the design of electrically heated melters operating at high power.
- o A sol/gel technology for producing glass microspheres for analytical particulate standards is being explored. The technique consists of spraying aquasols into droplets and transporting these droplets through successive zones of increasing temperature for drying, removal of residual volatiles, melting and fining. A prototype apparatus is under construction and several stable aquasol precursors for one target compositions were synthesized.
- o NBS in joint work with the Materials Characterization Center at Battelle, Richland, WA, provided for the acquisition of glass to be used as a standard for leach test calibration measurements. Melting and property tests were performed at NBS to assure that the glass met stringent specifications.
- o Four luminescent materials were developed for the U.S. Postal Service for use as primary standards in a new calibration device under development by USPS. Ten sets of these standards were delivered to USPS.
- o A systematic study was completed on simple borate glasses containing Yb. Retained water, chemical durability, UV-transmittance and general glassforming ability were determined. The optical properties of such glasses have potential for lasers which, however, is limited by their low chemical durability. It was found that chemical durability could be improved by the addition of Zn and La.
- o Thin films composed of 100% ZrO_2 and co-evaporated mixed films of 75% ZrO_2 :25% SiO_2 were prepared. Their total hemispherical light scatter was compared. The results show that the evaporated films have one-fifth of the scatter of the pure ZrO_2 films. The scatter

measurements correlate with x-ray diffraction measurements in which the 100% ZrO_2 films exhibit diffraction peaks, indicating polycrystallinity, whereas the co-evaporated mixed films show no such peaks. Crystallinity is believed to be one of the causes of the high scatter and optical loss of many thin films. These results point toward a means for creating improved films by co-evaporation.

- o The investigation of co-evaporated ZrO_2 - MgO films has been completed. Such films exhibit amorphous structures similar to ZrO_2 - SiO_2 films except that SiO_2 is more effective in inducing amorphous structure than MgO .
- o The optical characterization of thin films has been facilitated by a new theoretical analysis of the refraction of light through a prism. In this treatment the refraction of light through a prism for an arbitrary angle of incidence can be represented by an ellipse. The representational ellipse yields simple geometrical interpretations for total internal reflection, minimum deviation, and wavelength dispersion. The useful operating range of a prism coupler is given by the portion of the representational ellipse that appears within a window determined by the mode propagation conditions of the waveguide system.
- o An automated apparatus for the measurement of stress-strain behavior of thin films was designed, constructed and evaluated. The influence of bulge hole size, shape and film preparation technique of gold and aluminum films upon the measurement parameters was investigated.
- o In collaboration with the Metallurgy Division the first stages of an investigation into the microstructure of passivating films on metal were completed. Vapor deposited iron films were treated with passivating chromate and nitrate solutions. Investigation of the films in situ using the Cornell High Energy Synchrotron Source (CHESS) surface extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) showed that the chromate passivation produced films which are more vitreous. Since this treatment incorporated some chromium the results were interpreted as being due to the glassforming nature of chromium oxide.
- o An investigation of several spontaneous fractures of tempered glass plate enclosures at the Hart Building (Extension of the Dirksen House Office Building) was carried out at the request of the Architect of the Capitol. In one case where fragments could be recovered, fracture origin was determined and a microscopic nickel-sulfide inclusion was found at fracture origin. Nickel-sulfide is known to undercool to an unstable high temperature modification in the tempering process. A volume increase associated with a delayed phase transformation can cause spontaneous fracture.

Physics and Chemistry of Glass

Subtask 1

W. K. Haller, D. J. Cronin, A. Feldman, L. H. Grabner, D. A. Kauffman,
C. M. Scarfe,¹ M. E. Wilke

¹ Guest Worker from the University of Alberta

Kinetics of Heterogeneous Nucleation in Glass

The nucleation behavior of glasses is of interest in glass science as it is frequently the controlling factor in glass formation. Also, the controlled nucleation of glasses allows production of dense fine grained ceramics.

In the past year a study of the heterogeneous nucleation behavior of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass has been concluded. Platinum particles were used as the heterogeneous nuclei. Earlier workers had reported in the literature that the effectiveness of platinum as a nucleating agent was a function of platinum concentration in lithium silicate glasses.

In the present study the number of platinum particles and the number of crystals were determined by independent techniques. The results showed excellent agreement between the number of platinum particles and the number of crystals. This shows that all platinum particles do, in fact, act as nuclei yielding individual crystals. It was also found that for certain glass preparation conditions the number of platinum particles formed would first increase with increasing platinum concentration, and then decrease as platinum concentration was further increased. This effect could account for the reported concentration dependence of the nucleating ability of platinum particles.

Analysis of nucleation rates also showed no dependence on platinum concentration. It was found that the nucleation rates could be described well using classical nucleation theory. This is in contrast to the case of the homogeneous nucleation of lithium disilicate. Data in the literature for homogeneous nucleation of $\text{Li}_2\text{O}-2\text{SiO}_2$ show large discrepancies from behavior predicted by classical nucleation theory. The reasons for such discrepancies are not known. Analysis of the data from the literature indicates that the nucleation process is more complicated than expected and cannot be treated as a single simple activated process over the entire temperature range studied.

The work has been published in the form of a Doctoral Dissertation by D. J. Cronin ("Heterogeneous Nucleation of Lithium Disilicate Glass," Alfred University, Alfred, NY, May 1983).

Dynamic Synchrotron SAXS Investigation of Subliquidus Phase Separation

The purpose of this investigation, conducted in collaboration with G. B. Stephenson and A. I. Bienenstock of Stanford University, is the in situ observation of the early stages of the metastable liquid/liquid phase separation in glasses. This phenomenon has been widely studied in the past, mostly by electron microscopy on chilled glass samples having

undergone various thermal histories. Through these post-mortem investigations much has been learned about the kinetics of the phase separation process. The availability of a high intensity x-ray source, together with sensitive advanced detectors which can collect meaningful scattering data over a short span of time, offered an opportunity to investigate in situ the early stages of phase separation. A disadvantage of the technique is the necessity of having good x-ray contrast between phases and the fact that, at best, one obtains only a kinetics of the development of average size of scatterers, in no way rivaling the detailed morphological information obtainable by high resolution electron microscopy of shaded replicas of fractured and etched surfaces.

Since the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system, widely studied by other techniques, did not provide sufficient scattering contrast, a phase-separating glass composition with a heavy element (Ba) had been developed. Good time resolved SAXS data were obtained and were analyzed during this year. The analysis indicated that the thermodynamic driving force of the early-stage approximation of the Cahn-Hilliard-Cook theory for spinodal decomposition was applicable, but that the kinetics do not obey the diffusion equation of the theory. To allow for this deviation, an extension of the theory was developed where internal stress effects during decomposition are considered.

Monitoring of phase-separation by SAXS provided an elegant demonstration of the reversibility of the process. In a $\text{Na}_2\text{O}-\text{SiO}_2$ glass, it took less than five seconds above the critical temperature to dissolve previous phase separation.

The work has been published in a doctoral thesis by G. B. Stephenson ("Early-Stage Phase Separation in Amorphous Solids: A Time-Resolved SAXS Study," Stanford University, Stanford, CA, January 1983).

Viscosity and Structure of Low Alkali "Mineral Glasses"

As part of a continuing study in collaboration with Dr. C. M. Scarfe, of the University of Alberta, Canada, a systematic study of melt viscosities in the diopside-albite-anorthite ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2 - \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 - \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) ternary system was carried out. The objective was two-fold: to provide high quality viscosity data on these compositions and to use the viscosity data in conjunction with vibrational spectroscopy data to obtain information relating to melt structure. From a practical standpoint, "mineral glass" compositions are interesting because of their high resistance against alkaline attack, their high electrical resistance and their low cost. This makes them potential candidates for glass fibers (concrete reinforcement), and electric insulators.

Earlier work had focused on the diopside-anorthite join and the diopside-albite join. The diopside-anorthite work has been described in a paper to be published in the September 1983 issue of American Mineralogist. The diopside-albite work is described in a paper currently in review process.

Over the past year viscosity data for eleven compositions in the ternary systems have been obtained. Initial analysis of the data shows certain

systematic variations. For a constant diopside concentration the viscosity at a given temperature decreases as anorthite replaces albite. For a given diopside concentration the range of viscosities increases as the diopside concentration decreases. Also, for a given albite/anorthite ratio, the viscosity at any given temperature increases as the diopside concentration decreases. These general trends are expected from previous work and what is known of the melt structures of the end members. Albite and anorthite are reported to have three dimensional network type structures while diopside is reported to be a completely depolymerized structure consisting of individual structural units. Therefore, addition of diopside tends to break up the network and lead to a decrease in viscosity. Vibrational spectroscopy studies of these glasses will be carried out at the University of Alberta. A more detailed analysis of the viscosity data is also in progress.

Piezo-Optics

Zirconium fluoride glass is one of a series of heavy metal glasses that are of current research interest because of their extended transmission range into the infrared as compared to conventional oxide optical glasses. This is because of their potential use as infrared transmitting fibers. Furthermore, their extended infrared transmittance suggests that their absorption will be low at shorter wavelengths as well. Because of this interest, and upon request by the Naval Research Laboratory, piezo-optic measurements on this material were conducted. The piezo-optic constants, q_{11} and q_{12} , and the elastic constants, c_{11} and c_{12} , were measured. In addition, the coefficient for stress-induced birefringence, $q_{11}-q_{12}$, was measured as a function of wavelength from 0.6 μm to 5 μm . An important result found was that measured values of $q_{11}-q_{12}$ were approximately 5 percent of the value of $q_{11}-q_{12}$ for fused silica. Thus, this material exhibits a very small stress birefringence. Two implications of this result are: polaroscopic examinations of this material will be insensitive to the presence of large internal strains; optical components made from this material will maintain isotropic properties in spite of strains present.

A compilation of the piezo-optic and elastic constants of approximately 75 transparent materials was completed. This compilation will appear in the Handbook of Laser Science and Technology, to be published by the CRC Press.

Standard Reference Materials for Glass Processing and Use Subtask 2

W. Haller, M. J. Cellarosi, D. J. Cronin,

Glass Dielectric Constant SRM

The certificate for this SRM was published this year, and the lead silicate glass representing this standard (SRM 774) is now on sale. This SRM is especially important to the glass industry and users of glass for checking test methods and to calibrate equipment for the determination of dielectric constant and related loss characteristics as a function of frequency. SRM 774, in particular, will aid R & D effort and further the advance of glass in electrical and electronic applications.

Glass High-Temperature Resistivity SRM

Development of a melt resistivity standard is now listed as a first priority by ASTM Committee C14 on Glass and Glass Products.

Accurate melt resistivity data have major cost implications in glass melting as the information is used to minimize power usage at maximum production. There is an increasing trend in the glass industry to convert oil fired operations to modern electric melt facilities because of the significant economies resulting from energy savings and better quality coupled with longer furnace campaigns and substantial reduction of pollution emissions. For these reasons, the glass industry through ASTM and NBS have begun the certification of a glass SRM for high-temperature resistivity and related methods.

NBS and three industrial laboratories have so far been cooperating in comparison measurements within the scope of generating a standard and related methodology. Glass viscosity SRM 711 and high-temperature viscometry procedures have been used to generate data. KCl aqueous solutions provide the reference calibrations for cell constant determinations.

A statistical analysis of data collected so far indicates an agreement of within 5 percent among the laboratories with a correlation coefficient of 0.99. These results were obtained after procedure improvements recommended by NBS were accepted by the cooperating laboratories. Previously discrepancies of the order of 30 percent existed in the very high temperature range.

Viscosity SRM

NBS Glass Viscosity SRMs have an important role in glass research and manufacture. Viscosity and temperature relationships are used in all stages of the manufacturing process, and in advanced technical applications such as in glass-to-metal and glass-to-glass seals.

The glass industry relies on NBS to provide the essential long term supply of glass viscosity standards. At present, the inventory of viscosity SRM 710 (Soda-Lime-Silica Glass) is projected to last until 1984. Plans have been made to replenish and improve this standard. This project requires about 1000 kg of glass of high homogeneity. Interlaboratory comparison measurements will be carried out at NBS in collaboration with industrial laboratories and ASTM Committee C-14 on Glass and Glass Products. In conjunction with the re-issue of SRM 710, NBS plans the completion of a new precision viscosity facility to expand the range of measurements and increase precision.

Other SRM Development Activities for the Glass Industry

The glass industry requested a thermal expansion standard for soda-lime-silica glasses, which has $\sim 9 \times 10^{-6}/^{\circ}\text{C}$. NBS presently does not provide such an SRM. Available glasses so far examined have shown a thermal history effect and a search is in progress to find glass compositions without such an effect. If such a glass is not identified, available Kimble R-6

soda-lime glass which has already passed homogeneity evaluations, will be used with prescribed measurement methods.

A new candidate material for a high alumina sand chemical SRM for the glass industry was finely ground and mixed. XRF measurements were carried out and acceptable homogeneity was proven. Samples were distributed and interlaboratory testing on chemical analysis is in progress.

Soft borosilicate glass for analytical standards supplied by Manville Corp. was ground and molded by Corning's Clearform process. XRF checks indicated acceptable homogeneity. The samples were distributed and interlaboratory testing on chemical analyses is in progress.

A glass with total iron content of 0.05 to 0.15 percent and ferrous/ferric ratio of 0.5 to 1.0 is required as a glass standard for ferrous/ferric ratio. Consensus activities on methodology are in progress utilizing the results of measurements performed on NBS SRMs 620, 621, 1830, and 1831.

Three glasses were identified for certification as candidates for glass density standards: Kimble R-6 (Soda-Lime, $\rho = 2.5$ g/ml), SRM 739 (borosilicate, $\rho = 2.3$ g/ml), and SRM 711 (lead glass density: 3.6 g/ml). Sample preparation and measurements are in progress.

A supply of Corning 9606 glass-ceramic in storage at NBS Boulder is under investigation for possible use as a thermal conductivity standard. Tentative measurement procedures have been identified.

Fused quartz annealing point and strain point standards are under development. Data on GE-fused quartz did not show an acceptable match and the problem was identified as procedural. Retesting is in progress.

Other candidate SRMs for analytic use by the glass industry are under study: borate ore; fluorine opal with CaO ; glass with 20% TiO_2 .

Glass Standard Reference Materials Liaison

Close relationship with the glass industry and other research organizations on the technical/scientific aspects of glass were maintained. Also maintained was active participation on ASTM Committee C14 on Glass and Glass Products and other standards organizations.

Many technical inquiries on glass SRMs were answered. We also carried out reviews of methods, selection and distribution of materials/procedures, data analysis, and organization of official ASTM meetings/activities.

Glass Standard Reference Materials for Other Industries

Subtask 3

W. K. Haller, D. H. Blackburn, M. J. Cellarosi, D. J. Cronin, A. Feldman, L. H. Grabner, M. E. Wilke

Glass Standards for Small Particle Chemical Analysis

The fact that glass is a most homogeneous, structureless solid has made it a choice material for analytical standards in elemental analysis. NBS has, in the past, issued a considerable number of such glasses as Standard Reference Materials, not just for use by the glass industry but also for the ever growing community of analysts using emissive techniques such as x-ray fluorescence, etc.

The analysis of small particulates poses a special problem. Here again, glass analytical standards, in addition of having the above stated advantages, offer easy formability into particles with one or more small dimensions. In the past, the Glass Section has produced glass fibers, irregularly shaped particles and glass spheres. Usually bulk-glass pieces of identical compositions are provided for comparison purposes.

The mentioned glass fibers were made by drawing, i.e., pulling a fiber from a melt through an orifice. Glass spheres were made by crushing and screening bulk glass into a powder of irregular shaped particles, followed by blowing the powder through the hot zone of a tube furnace where the particles melt and, due to surface tension, assume spherical shape. Another shape of interest for SRMs are thin films produced by sputtering from targets provided by the Glass Group.

During the past year, work on this project was continued in two areas:

1. Several bulk and spherical particulate glasses were provided to the Analytical Chemistry Division of the NBS. A talk on previously made SRMs, entitled, "Glasses for Microanalysis: New NBS Standard Reference Materials" by R. B. Marinenko and D. H. Blackburn will be given in September 1983 at the International Congress on X-ray Optics and Microanalysis in Toulouse, France. The construction of a facility to melt, crush, screen, and levitate melt glasses containing radioactive isotopes was continued.

2. Work was begun toward the development of a new technology, consisting of producing an aerosol by spraying of an aquasol and transporting the droplets through increasingly hot zones for drying, removal of residual volatiles, melting, and fining. This activity will eventually lead to the production of submicron glass spheres.

A prototype apparatus, using a gas propelled venturi sprayer with four heating zones and a melting furnace, was constructed and instrumented. It is presently undergoing testing. Furthermore, work to synthesize aqueous sol precursors for one target composition was undertaken. Several chemical approaches were undertaken and one pathway has so far produced a sol which appears to have sufficient stability. Problems connected with the non-Newtonian behavior of the colloidal dispersion are presently being investigated.

Nuclear Waste Leachability Research Material

To aid the U.S. nuclear waste program, the Material Characterization Center (MCC) at Battelle Northwest Laboratories requested the assistance

of NBS in the development and acquisition of a glass to be used as a standard in the calibration of leach test measurements. The glass composition was developed in cooperation with the MCC. Tests at NBS were performed to assure that the glass composition could be produced on a commercial scale. The Glass Group assisted in writing the purchase specifications and provided technical advice throughout the procurement process. The glass has been received at NBS and is currently undergoing tests to assure that the glass meets specifications. It will then be turned over to the MCC for distribution.

Fluorescence Standards for Automatic Postal Canceling Machines and Non-destructive Testing

Over the past year two development projects were undertaken for the U.S. Postal Service (USPS). The first involved developing luminescent materials for use as primary standards for a new calibration device being developed by the USPS. These required a green phosphor, red phosphor, red fluorescent of specific characteristics and one material showing no fluorescence. The red phosphor and red fluorescent material were produced using a europium doped soda-lime-silica glass. The nature of the green phosphor specifications resulted in using a commercially available phosphor, Mn doped zinc silicate, in a sintered glass matrix. The material chosen for the standard having no emission was $Y_5Fe_3O_{12}$ (garnet).

The success of the first standards resulted in a second project to develop materials to be used in calibrating automatic canceling devices on a routine basis. This requires a thin material that can be mounted in a carrier and fed through the canceling device simulating a letter. The standard must have stable luminescent properties, good mechanical durability, and a smooth surface that can easily be cleaned. Glass enamels on a metal substrate were chosen as the material for the standard. This promises to produce a standard that is much more durable and stable than the present standards at less than one tenth the cost.

A commercially available enamel, which has been remelted to incorporate europium, appears to be satisfactory for the red fluorescent standards. Work is continuing on the green phosphor material. A commercial phosphor, as mentioned above, is being used. This is encapsulated in a commercial enamel designed specifically for use with phosphor.

The enamels are applied to a pre-enamelled metal blank having a total thickness of 0.020 inches. Tests of the enamel standards on actual canceling devices have proven very successful.

In associated work for the Center for Analytical Chemistry, a glass was designed and produced that can be used as a standard for calibrating the fluorescent intensity of dye penetrant materials in non-destructive testing. The glass is a sodium-aluminum phosphate with Tb_2O_3 as the fluorescent species.

Refractive Index Standards

At the request of the NBS Office of Standard Reference Materials, work was completed on a revision of a document for the International Union

for Pure and Applied Chemistry (IUPAC), Physical Chemistry Division, Commission on Physicochemical Measurements and Standards, entitled: Recommended Reference Materials for Realization of Physicochemical Properties; Optical Refraction (Refractive Index). In order to accomplish this task, the following actions were taken: (1) A survey of presently listed suppliers was made to ascertain whether standard reference materials were still available. (2) The availability of current NBS standards was ascertained. (3) A survey of other potential suppliers of refractive index standards was made. (4) A revised draft of the document was prepared for IUPAC consideration.

Glass Processing Subtask 4

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Laser Glasses

The Glass Group has had a continuous collaboration with Lawrence Livermore National Laboratory (LLNL) for a number of years. The collaboration has involved development of experimental glasses for use in LLNL studies of the lasing process.

A total of 61 successful glasses were made over the past year and submitted to LLNL for testing of lasing properties. In addition, an extensive study of borate glasses was undertaken at NBS. This study involved an investigation of physical, chemical and optical properties of borate glasses containing Yb. The objective was to determine the effect of composition on lasing properties of Yb in borate glasses and to determine promising compositions that might be of commercial interest.

Several properties were of interest in addition to lasing properties measured at LLNL. These included the ability to suppress devitrification on processing, control of water content, UV transmittance and chemical durability.

It was found that bubbling CCl₄ through the melt decreased the water retained in the glass. Addition of LiCl also reduced the water content. It is known that the addition of fluorides to silicate glasses decreases the water retained in the glass, however, in the borates the addition of fluorides resulted in a slight increase in water retention. The addition of halides of any sort led to very inhomogeneous glass that suggests such techniques could not be used for making a product of optical quality. Systematic composition studies showed that the Li borate glasses retained less water than the sodium borates. For the alkaline earth borates the amount of retained water increased with decreasing atomic weight, Ba → Mg.

Two types of chemical durability tests were used. One involved determining weight loss of polished specimens immersed in distilled water at 25 °C. The second measured hygroscopicity in a 90 percent relative humidity atmosphere at 25 °C.

The immersion tests for the alkali borates and alkaline earth borates showed that glasses containing elements of lower atomic weights are more durable. The alkaline earth borates were superior to the alkali borates. The durability of any of these borates, however, is inferior to a commercial container or architectural glass. Two borate glasses seemed to have acceptable durability. These were a binary zinc borate and a lanthanum borate glass. They showed minimal weight losses and no surface degradation.

The high humidity tests showed that the binary alkali borates have poor resistance to high humidity conditions, the sodium borate more so than the lithium borates. The alkaline earth borates showed negligible weight gains under the test conditions and only minor surface degradation. The La and Zn borates showed no surface degradation throughout the tests.

The correlation between the immersion tests and high humidity tests is complicated by several factors. Within a given group, such as alkali borates or alkaline earth borates the relative ranking of glasses seems to be the same for both tests. However, comparison of glasses arbitrarily can be misleading. For instance, in immersion tests the barium borate glass shows a rate of weight loss greater than that for the lithium borate glass, but in high humidity the attack of the lithium borate glass is much greater than the attack of the barium borate. Therefore performance in one type of durability test is not always a good indication of performance under other conditions.

From the standpoint of optical properties a low refractive index is desired thus requiring low atomic number elements. It appears that suitable glasses could be developed in the borate system using the lighter alkaline earth borate as a base with a minimum of alkali. Zinc borate would also provide a good starting point because of its superior durability.

Results of the optical part of the study are to be published in the Journal of Quantum Electronics.

Low Loss Films for Integrated Optics

The development of low-loss optical fibers has triggered a new technology in which optical fibers are now being used in place of traditional electronic and microwave communication links. However, the signal processing before and after the optical transmission is still done electronically, which limits the ultimate frequency responsivity of the system. The full realization of the advantages of optical communications requires the development of means for direct processing of the optical signal and this new technology is integrated optics. The role of the Glass and Optical Materials Group in this area is:

1. Research to support the development of new low-loss thin film materials of potential application in integrated optics.
2. The fabrication of planar waveguides with carefully controlled mode structures for minimizing coupling losses due to mode mismatch between integrated optical components.
3. The search for new materials and thin film structures that show enhanced nonlinear optical coefficients with the view toward applications in integrated optics.
4. The development of consensus standards, in cooperation with industry and government, for characterizing and evaluating materials for integrated optics.

The work during the previous year falls under the first two categories.

Planar waveguides made by thin film deposition process have attenuations or losses which are several orders of magnitude higher than that of optical fibers made from glass. While the exact mechanisms contributing to these losses are not fully clarified, workers agree that a significant source of loss is caused by scattering. Scattering occurs on discontinuities in the films. Discontinuities are pores, grain boundaries (deposited waveguides are mostly polycrystalline) and columnar structures which can frequently be seen in electromicrographs.

Some time ago, NBS proposed to eliminate one source of scatter by making waveguides which are vitreous rather than polycrystalline. Using pure glassformers such as SiO_2 was not possible because of the requirement for a high refractive index. On the other hand, it was known from the synthesis of bulk glasses, that metastability (glass formation) could be obtained by adding relatively small amounts of glassformers to other non-glassforming constituents or by discouraging crystal growth by the mixing of several non-glassformers in ratios which are outside of primary crystallization fields.

Applying the above principles, NBS produced films by coevaporation of non-glassformers (ZrO_2) with minor additions of glassformers (SiO_2) and also by coevaporating two non-glassformers (ZrO_2 , MgO). It was found and reported that the addition of 21% SiO_2 to ZrO_2 (fig. 1) and the addition of 46 mol% MgO to ZrO_2 produced films which were devoid of crystallinity peaks in x-ray diffraction. Also, in high magnification SEM, the amorphous films did not show any columnar structure.

In the past year the characterization of the coevaporated optical thin films was continued. An apparatus was constructed which measures the total hemispherical scatter from a thin film specimen illuminated normally with a helium-neon laser beam. A schematic diagram of the apparatus is shown in figure 2. The apparatus measures light scattered back from the specimen within a 2° solid angle, less a 3° cone centered on the optic axis. A portion of the specimen is masked so that some of substrate remains bare. The scattered signal is measured as a function of position on the specimen by traversing the specimen through the optical beam; for comparison, measurements are also performed on the

uncoated substrate. In order to minimize signal arising from the bottom surface of the substrate, the specimen is placed on a black glass plate with an index matching fluid in between. Computer control of this apparatus is currently under construction.

Figure 3 shows the scatter profiles of two specimens. The film on specimen number 1 is a pure zirconium oxide; the film on specimen number 2 contains 75% zirconium oxide/25% SiO_2 . Specimen number 1 shows 5 times the optical scatter of specimen number 2. X-ray diffraction (fig. 1) has already shown that the film in specimen number 2 is amorphous whereas the film in specimen number 1 is polycrystalline; thus the amorphous film shows significantly lower scatter than the polycrystalline film. Experiments are continuing on a series of $(\text{ZrO}_2)_x(\text{SiO}_2)_{1-x}$ films with varying values of x .

The work described necessitated several instrumental developments to characterize the films during and after the deposition process. An optical path monitor was incorporated into the deposition chamber. Here, a laser beam is incident on the substrate surface. The reflected beam is monitored during deposition and from the turning points in the recorder trace of the reflected intensity the optical path can be determined. This enables one to monitor films while depositions are proceeding. Information on the index of refraction and density can be extracted from the optical path data and can be correlated to deposition rates and substrate temperatures. A set of measurements on ZrO_2 and SiO_2 has been completed. Measurements on mixed films and films formed at different temperatures and rates will be made.

The prism coupler is the means for coupling light into optical waveguides. From a determination of the angles required to couple into all the waveguide modes, one can calculate the effective refractive index of each mode. The data allow for an accurate determination of film refractive index, thickness, and birefringence. In the case of graded index layers, estimates can be made of the index distribution. While implementing the use of a prism coupler for measuring light propagation in thin films, a new way for describing prism-coupling was discovered. This is based on a graphical method, developed within the group, for describing prism refraction. Consider a light ray propagating through a prism, apex angle A , situated in air. The functional relationship between the sine of the incident angle and the sine of the exit angle, each measured with respect to its respective face normal, is an ellipse with ellipticity $\tan A/2$. The ellipse representing any prism of refractive index n_p can be inscribed in a square, $2n_p \times 2n_p$, where the principal axes of the ellipse lie along the square diagonals. The ellipse is tangent to the square at four points; the four segments of the ellipse so determined represent refraction through the four adjacent-face pairs of a biprism. The conditions for total internal reflection, minimum deviation, and wavelength dispersion have simple geometrical interpretations on the basis of the ellipse representation. The elliptical relationship still holds when the treatment is extended to a prism with media of different refractive indices on opposite sides. This case applies directly to prisms used for coupling radiation into thin film waveguides and can be used to predict the useful operating range of a prism coupler. It is given by the portion of the representational

ellipse that appears within a window determined by the mode propagation conditions the waveguide system. A schematic diagram of the prism coupler and a graph of the ellipse representation of prism refraction, as applied to the prism coupler, is given in figure 4.

Fluoride Glass Fibers for Light Guides

While silica glass fiber communication links are slowly becoming a part of public technology, materials development in the fiber field is continuing. Until recently, the most important development in silica-based fibers was the reduction of light absorbing impurities in the glass, together with the enforcement of utmost cleanliness to exclude foreign light-blocking particles. Vapor-phase deposition inside of glass tubes has become the choice technique for making such silica-based fibers. Impurity levels have been reduced to such an extent that they are no longer the factor which controls light attenuation. Fibers with an attenuation of 0.2 dB/km have been made whereby intrinsic Rayleigh scattering of the glass becomes the dominant loss mechanism within the optimal transmission range. Since Rayleigh scatter is strongly wavelength dependent, further reduction in loss can be expected from operating the fiber links with light of longer wavelength, which, however, is not possible with silica-based fibers because of multiphonon absorption in the infrared region. The replacement of oxygen by fluorine in glasses shifts the multiphonon absorption to longer wavelength and heavy-element fluoride glasses are presently at the center of interest of the fiber optics community striving for a second generation fiber optics material.

The problems in making fluoride glass fibers are manifold: steep viscosity curves of the melts cause problems in fiber drawing; interference of outright and/or incipient crystallization; reaction of the melt with oxygen and water vapor; vaporization of high vapor pressure melt components; poor chemical durability of fluoride glasses; and finally, the difficulty to obtain the needed fluoride raw material in sufficient purity and, in particular, free of oxides.

While the presence of large amounts of oxygen in the fluoride glasses is obviously detrimental, quantitative correlations of optical performance and oxygen content have so far been hindered by the difficulty of analyzing a fluoride glass for small amounts of oxygen.

The Naval Research Laboratory, which is heavily involved in fluoride fiber research, has recently asked NBS for help in the oxygen analysis problem. The use of two different tools for oxygen detection is planned. One is electrochemical determination of oxygen activity in the molten glass with an oxygen responsive zirconia membrane, the other is by way of ESCA of glass samples. The success of the first approach depends upon the oxygen selectivity of a solid state electrolyte and it has first to be established that the excess of fluorine does not interfere with the oxygen response. Construction of the zirconia membrane sensor is in progress.

The second approach plans to use the thin film synthesis/analysis facility of the Division. Glass samples will be introduced into the vacuum chamber, and a fresh surface will be created either by fracturing in the vacuum or by ion etching. Oxygen will then be detected by ESCA

analysis. Since our ESCA apparatus samples over a wide area of the specimen, the ion etched area and the analyzed area have to be carefully aligned. Presently, work is underway to do this.

Glass for Dental Prosthetic Uses

Because of its high chemical durability, its ability to be shaped by thermoplastic means and the ability to achieve coloring and opalescence effects, glass has had some special attraction to the designers of dental restorative and prosthetic materials. Several years ago, the Glass Section had been involved in a collaborative development with the NBS Dental Group dealing with cosmetically, chemically, and mechanically satisfactory cements to fill cavities of the frontal surfaces of teeth. The developed cement, today widely used commercially, consisted of tightly packed glass particles bonded by a high polymer phase. For proper functioning, a glass of very specific thermal expansion, refractive index and good chemical durability had to be developed. It was also desirable to impart x-ray opacity at low toxicity in order to enable inspection for secondary caries.

More recently, the Glass Group has been involved in a new study relating to prosthetic, rather than restorative materials. Gold or stainless steel prosthetic devices usually carry a plastic or ceramic facing which looks and functions like the missing tooth. A more recent variation of such a structure uses glasses, which are directly bonded to the metal part of the bridge. For the purpose of shaping and also to achieve the opalescence of a tooth, the prosthesis is made by fusion sintering of glass powders. In the ongoing program, the Glass Group has synthesized several glasses of proper thermal expansion and viscosity for fusion onto the metal parts. It is planned to enter into a more extensive program where viscosity, thermal expansion, and chemical durability of the glass will be tailored for optimal performance. Eventually, glass will be in the form of microspheres of a predetermined size distributions to obtain close packing in the molding stage. Such spheres will be produced by spraying and levitation melting of aquasol precursors of glasses.

Mechanical Properties of Ceramic Thin Films

Subtask 5.

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Reactive Fracture in Silica

An understanding of the influence of stress on the kinetics of reactions which lead to delayed failure in ceramic materials is necessary to develop a theory to quantitatively predict such behavior. During the last year an attempt was made to obtain this data by using thin films to model the material under high tensile stress immediately in front of the advancing critical flaw. Conceptually, thin films provide a means of

obtaining unreacted surfaces of a desired material which can be stressed to extremely high levels by deforming the underlying substrate materials.

Based on vacuum fracture experiments made earlier and on slow crack growth results, SiO_2 was chosen as the model system and ammonia as the reactive environment. These earlier experiments showed that silica experienced slow crack growth in an ammonia environment quite similar to its behavior in air containing water vapor. In addition, the nitrogen in the adsorbed ammonia molecule could be monitored using ESCA.

Initially, a thin metal plate was used as the substrate. This substrate was cut to have a cross section so that when supported at one end and deflected at the other, a uniform tensile stress could be produced in the film. The plate was fabricated from a Be-Cu alloy so that it could withstand stresses of some 100,000 psi without undergoing plastic deformation. A thin film of SiO_2 was next deposited onto this substrate using electron beam evaporation of the oxide. The residual oxygen pressure was purposely held to values in excess of 1×10^6 torr in order to prevent reduction of the oxide.

In a second approach a coating of SiO_2 was deposited on a mylar film which was in turn held in a jig which allowed the mylar to be stretched while still under ultra-high vacuum conditions. In this case the SiO_2 was produced in two ways. First, by SiO_2 evaporation as in the case of the Be-Cu substrate and second, by reactive evaporation of Si in an oxygen environment. The latter was attempted in order to allow for a Si inter face layer between the plastic and the oxide to promote adhesion. The mylar film experiment was employed because it allowed the SiO_2 to be subjected to greater tensile stresses.

While initial comparisons of differences in nitrogen peaks between stressed and unstressed films looked encouraging, indicating that the stressed films adsorbed ammonia more rapidly, more recent measurements cast doubt on these results. Specifically, it was found that unstressed thin films of SiO_2 could be produced which would adsorb significantly different amounts of ammonia as evidenced by the ESCA spectra. While the films in question were produced with nominally identical deposition conditions, apparently they differed in available adsorption sites. Currently a systematic study is being carried out on unstressed films prepared by different processing routes to establish the cause of such variations. At the conclusion of that study a determination will be made concerning the continuation of the thin film approach for studying stress enhanced reactivity. However, studies of the chemical species which are produced on surfaces which have been fractured in different environments and at different rates will be pursued.

Stress-Strain Properties of Thin Films

Studies of the mechanical properties of thin films such as protective coatings are important because such properties frequently limit the usefulness of films in practical applications. Properties of particular interest are the elastic modulus, the strength, the transition from elastic to plastic behavior and thin film creep. These properties in large part determine the ability of a coating to adhere to its substrate while undergoing mechanical and thermal stress.

During the last year an apparatus was constructed to measure stress-strain relationships of unsupported thin films using the bulge technique. In this technique, the deflection of the film is measured in response to an applied differential pressure across the film. The measurements were performed under computer control so that the stress and strain could be calculated instantaneously. This is necessary for the next stage in which the film will be subjected to a continuous stress while it undergoes time-dependent strain or creep.

In addition to apparatus development, several new techniques were evaluated for the production of unsupported thin films. The first involved using iodine vapor transport of masked portions of metal substrates to produce well defined areas of unsupported film. While attempts to transport metal proved successful, an unexpected surface roughening occurred. Because of this, efforts were redirected toward the current technique now to be described.

In the current approach, a thin film of 50-100 nm thickness of NaCl is deposited on a microscope slide. Next a film of the material to be measured is deposited. Finally, the latter is stripped from the slide using water and attached to the bulge tube. The attachment can be carried out after floating the film onto a water surface either by lowering the bulge tube from above or by raising the water level until contact is just made. A second approach involves gluing the bulge tube to the film while still attached to the microscope slide and submerging the whole unit under water. In this case the water intrudes under the film and separates the film from the slide. The first technique removes the effect of intrinsic film stress from the measurement while the latter technique permits the measurement of this effect.

Measurements to date have concentrated on the influence of bulge hole geometry and film processing on stress-strain relationships in gold and aluminum. The elastic modulus values calculated from the slopes are consistent with those reported in the literature. Sources of measurement uncertainty have been identified and are currently being rectified.

In the future, an electrically actuated valve will be installed to permit the control of the differential bulge pressure by the computer. In addition, a furnace will be installed to permit high temperature creep measurements of ceramic films produced by oxidation of the appropriate metals.

Metallurgical Thin Film Problems Subtask 6

D. M. Sanders and E. N. Farabaugh

Microstructure of Passivating Films on Metals

In the past year, collaborative work with staff members in the Metallurgy Division has been carried out. This involves research on thin films produced in our facility and studied using the synchrotron x-ray source that the National Bureau of Standards and the Naval Research Laboratory are developing jointly at the National Synchrotron Light Source at

Brookhaven Laboratory. Facilities for x-ray topography, small angle scattering, interface studies and crystallography will be available and preliminary experiments are being carried out in the Metallurgy Division and at the Cornell High Energy Synchrotron Source (CHESS).

One of the active areas of cooperation is in the structure study of passive films on iron. Here, 50 Å films of iron were evaporated by E-beam source on glass substrates. These were then passivated using either a chromate or a nitrite solution. While both solutions produce iron oxide films, those produced with the chromate solution were more vitreous and contained traces of chromium. The results are interpreted by the incorporation of chromium oxide, a glass-former, into passivated film.

Interfacial Structure of Multilayer Metal Films

Another area of cooperation is the study of multilayer materials. These are layer materials formed by depositing alternating layers of different materials several lattice spacing thick. They have practical relevance to superconducting structures and integrated optics and diffraction gratings.

As an initial investigation in this area, niobium films were deposited on copper single crystal substrates. These substrates were ion cleaned and annealed at 400 °C while still in the deposition chamber. A series of niobium films with thickness ranging from 500-1000 Å were produced with the aim to be the examination of the interface between the copper and niobium using synchrotron radiation. The initial experiments conducted at the CHESS facility were not as successful as hoped in that the annealing of the copper did not restore the surface to the degree of perfection necessary to observe the diffraction effects. This work will continue and further sample fabrication await the preparation of good copper substrates.

X-RAY DIFFRACTION SPECTRA

X-RAY SIGNAL

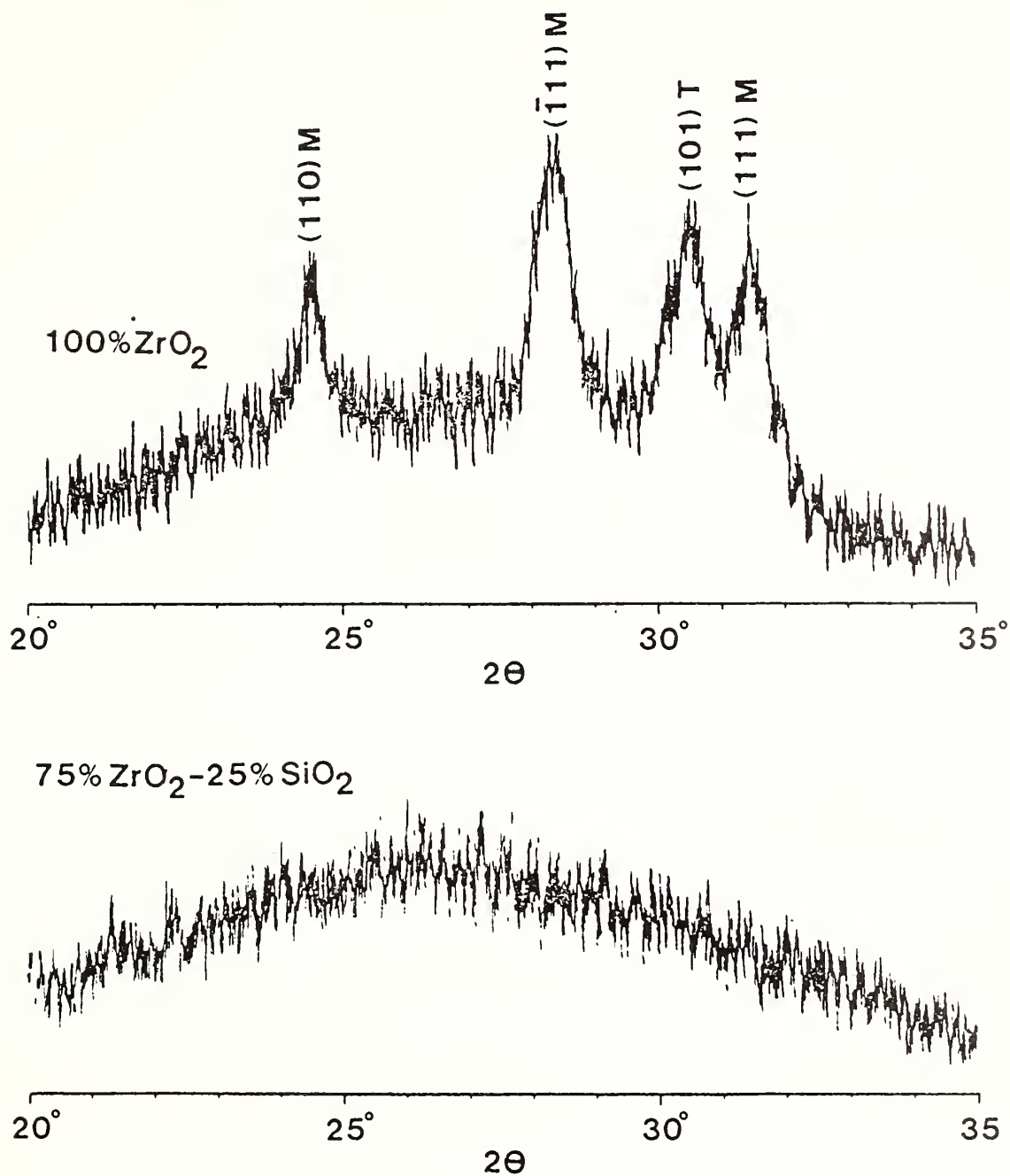


Figure 1 X-ray diffraction spectra of a pure ZrO_2 film and of a mixed $75\% \text{ZrO}_2/25\% \text{SiO}_2$ film produced by E-beam evaporation. The diffraction peaks present in the spectrum of the pure film indicate a polycrystalline structure. The absence of diffraction peaks in the spectrum of the mixed film suggests that the film is amorphous.

HEMISPHERICAL SCATTER FROM THIN FILMS

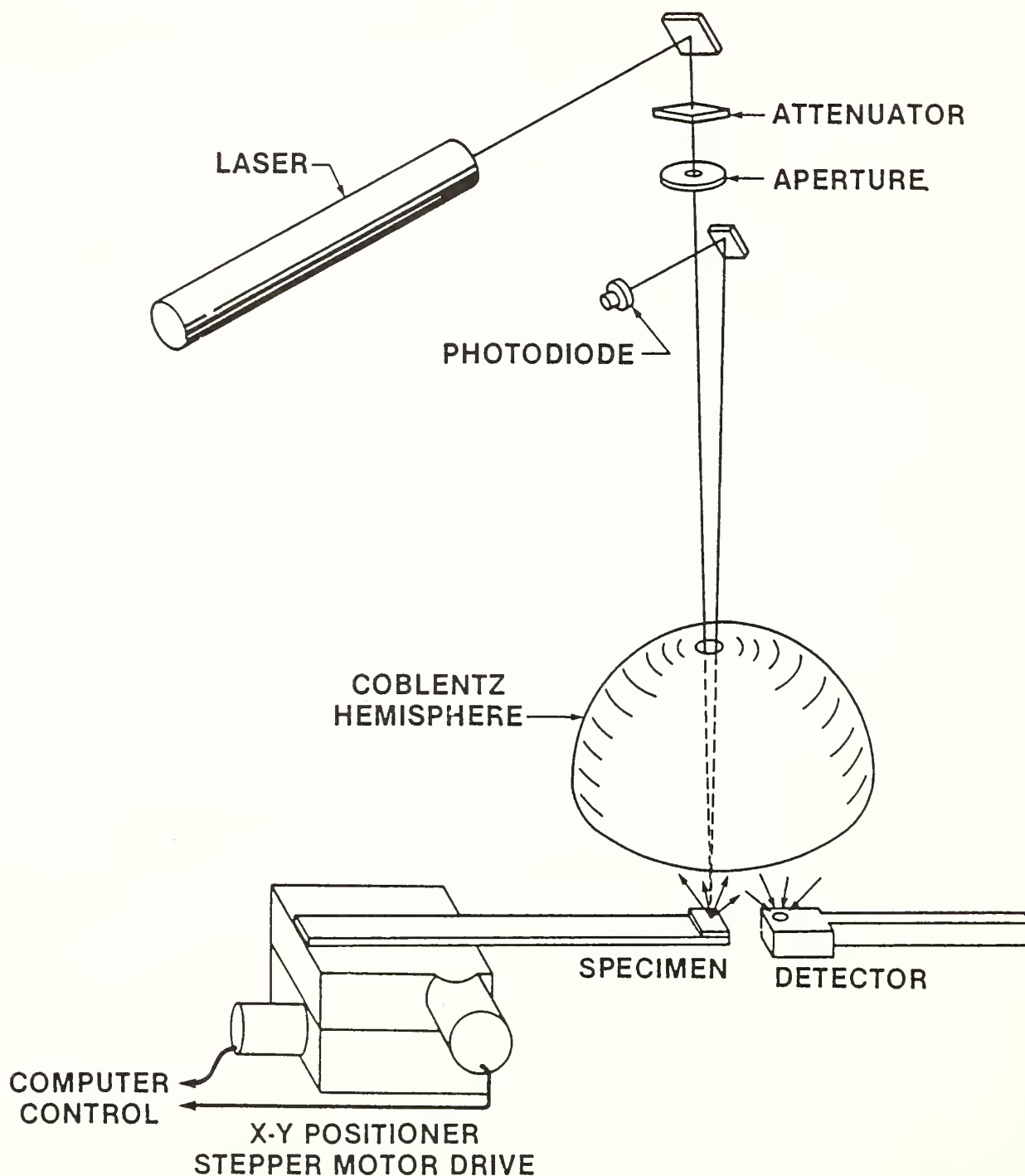


Figure 2 Schematic diagram of the apparatus for total hemispherical scatter. The computer control is under construction.

HEMISPHERICAL SCATTER PROFILES

FILM #1

100% ZIRCONIUM OXIDE

SUBSTRATE

FUSED SILICA

FILM #2

75% ZIRCONIUM OXIDE

25% FUSED SILICA

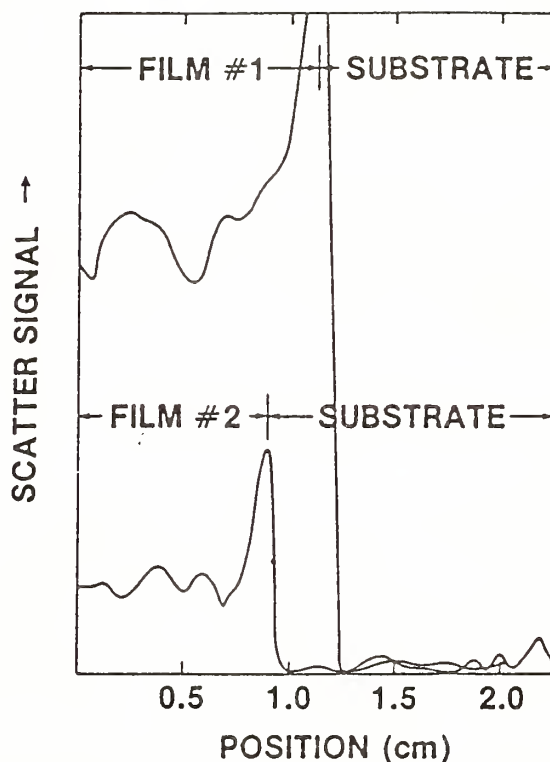
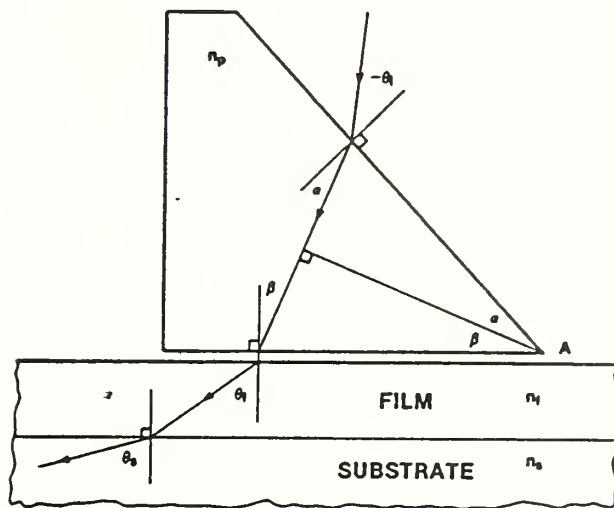
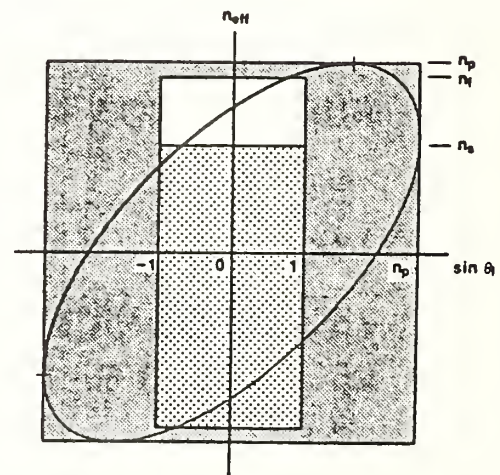


Figure 3 Preliminary experiments at CMS have shown that a film containing 100% zirconium oxide (Specimen #1) produces five times the optical scatter as a mixed film containing 75% zirconium oxide: 25% silicon dioxide. This result is illustrated in the figure, where the hemispherical scatter signal from both specimens is plotted as a function of position of the optical beam on the specimen. The specimens, prepared by electron-beam deposition, were masked so that the film covered only a portion of the substrate; the low scatter signals to the right are due to scatter from the bare substrate. X-ray diffraction studies indicate that the film producing the lower scatter is amorphous whereas the film producing the higher scatter is polycrystalline.

NEW WAY TO LOOK AT PRISM COUPLERS FOR INTEGRATED OPTICS



PRISM COUPLER/THIN FILM SYSTEM



ELLIPSE REPRESENTATION
WITH MODE WINDOW

Figure 4 A natural framework for evaluating the useful operating range of prism coupler is provided by a geometrical construction, recently discovered at CMS, in which refraction through a prism for an arbitrary angle of incidence is represented by an ellipse. The useful operating range is given by the portion of the representational ellipse that appears within a window determined by the mode propagation conditions in a planar waveguide. The figure to the right shows the representational ellipse; the mode propagation window is the clear rectangle in the upper portion of the figure.

3.5 MATERIALS PROCESSING AND DURABILITY CHEMISTRY

The objectives of this task are to provide data, measurement methods, and mechanistic understanding of chemically and biologically mediated processes that affect the processing and performance of inorganic materials. In this broad context, the experimental work of this task includes investigations of microbial corrosion, bioprocessing of materials, chemistry related to the environmental impact of the use of inorganic materials in service, and chemistry related to friction and wear. The work of the task is carried out under two subtasks, one dealing with chemical and biotransformations of materials, and one emphasizing tribology.

The chemical and biotransformations subtask has focused in FY83 on developing an improved understanding of the mechanisms of microbial corrosion to provide field methods for detecting and controlling this economically important source of materials degradation, and on fundamental research in support of innovative new antifoulant coating technology being developed by the U.S. Navy. New measurement techniques have been developed which are applicable to the biotechnology of metals processing and to monitoring the quality of the environment.

The tribology subtask is concerned with the development of test procedures for recycled oil in direct response to congressionally-mandated responsibilities of NBS in this area. The technical basis for procedures to determine the equivalency of virgin and recycled lubricants has been established, and the program is now in its final stages. New directions for this subtask have been established, and work has been started to investigate tribological (friction and wear) properties of advanced ceramic materials for applications such as adiabatic diesel and turbine engines, in cooperation with industry and other government agencies.

FY83 Significant Accomplishments:

- o Advanced measurement techniques were developed for molecular comparisons of organometallic polymers (OMPs) used in new Navy antifoulant paints. An extensively tested, laboratory synthesized OMP and an OMP synthesized using a new large-scale commercial process were shown to be of similar molecular composition. The work provides the Navy a basis for procurement of acceptable OMPs and avoids the need for lengthy field-testing.
- o A completely new theory has been developed to explain the mechanism of anaerobic corrosion of metals, a multibillion dollar problem in the U.S. Research using NBS-developed chemical speciation methods has shown that a volatile, phosphorus-containing compound which is highly corrosive to metals is produced by the action of sulfate-reducing bacteria on iron and steel. Phosphine is liberated from biologically corroded metal specimens upon acidification, and this may provide a useful diagnostic test for biocorrosion. These findings show the need for new methods in

detection and control of biocorrosion of metals and are being tested in a joint field study with the Department of Transportation on underground pipelines.

- o Computerized epifluorescence microscopy measurement techniques were developed for surface analysis of materials. The distribution of microorganisms (naturally fluorescing or dye-stained) which interfere with materials performance was mapped, and cellular fluorescence quantitated, using these techniques. This method makes possible the use of element-selective fluorescent dyes for non-destructive measurement of biological and chemical transformation rates on materials surfaces.
- o Methods have been developed to determine release rates of tributyltin molecules into salt water from wooden pilings treated by a new Navy-developed process for impregnating the pilings with protective biocidal organotin polymers. The new measurement methods permit measurement of release rates of organotin species within minutes of immersion, providing a basis to assess both effectiveness and environmental impact of the new treatment technology.
- o A method has been developed for simultaneous measurement of mercury and organotin species in environmental samples, to assess chemical processes that could result in the formation of toxic organomercury compounds in the environment. Measurements using this technique are being carried out in collaboration with academic and government laboratories.
- o Small angle neutron scattering (SANS) was applied for the first time to measure rates of metal accumulation by microorganisms. Cells accumulating uranium produced different neutron scattering spectra from cells not exposed to uranium; moreover, cells retained viability under neutron exposure. This result indicates that neutron scattering techniques can provide real-time information on bioprocessing of metals.
- o Toxic and strategic metals, supposedly tightly bound to sludge, industrial wastes, and polluted sediments have been shown to be readily solubilized by a common biogenic product, methyl iodide. Group-developed speciation methods showed that metal sulfides are rapidly solubilized by methyl iodide to produce methylsulfur gases and aquated metal ions. With SnS, methyltin (IV) forms by an oxidative methylation process. The results have great implications for environmental mobilization of valuable or hazardous metals and opens possibilities for metal ore bioprocessing.
- o Friction and wear test capabilities are being expanded to include the evaluation of ceramic materials. Modifications will allow testing at temperatures up to 1500 °C. A cooperative effort has been initiated with Cummins Diesel to evaluate high temperature friction and wear properties of ceramic components for the adiabatic diesel engine. A theoretical model is being developed for calculating contact junction temperatures for wearing ceramic pairs.

- o A novel test method to measure frictional properties of materials has been developed. The test procedure uses a wear-in phase with a model compound to produce constant surface roughness and contact area. The sample is then introduced and tested under constant film thickness. Results of this test have been shown to correlate with the ASTM five-car fuel economy test (\$30,000 per test). This test procedure has been submitted to ASTM for round-robin evaluation.
- o A theoretical model for the elastohydrodynamic (EHD) contribution in a lubricated four-ball wear contact has been developed. This model predicts the lubricant film thickness based on the contact area, the relative surface, the speed, and the load. This is the first time such a model has been developed.
- o In an effort to assess the effects of molecular structures on friction and wear, a polar subfraction isolated from a lubricating base oil has demonstrated low frictional properties. A procedure that separates base oils into molecular compound classes that show wide variations in antioxidant capacity and friction and wear properties were successfully demonstrated. As a result of this work, a cooperative study with two major oil companies has been initiated to examine the molecular compound type classes in the extracted phase of the base oil manufacturing processes.
- o A novel preparative liquid chromatographic separation methodology was developed that produces multigram quantities of molecular compound classes. This separation scheme uses clay, silica/alumina, and neutral alumina columns to separate complex hydrocarbons into distinct compound classes as measured by IR, MS, and C^{13} NMR.
- o The NBS developed Thin Film Oxygen Uptake Test (TFOUT) which correlates with the engine test has provided a key for determining the oxidation stability of automotive oils. An ASTM round robin on TFOUT has begun. TFOUT data from three NBS industrial cooperative programs have shown a significant correlation between lubricating oil composition and the oxidation stability of these oils.
- o A catalyst package for evaluating automotive oxidation stability of lubricants (SRM 1817) has been produced. The package contains an oxidized/nitrated fuel fraction and an oil soluble metal catalyst mixture. Certified values for oxidation induction times were determined by the TFOUT and Differential Scanning Calorimetry (DSC). Use of the catalyst package helps industries to avoid costly unnecessary engine tests.
- o Analysis of the extensive NBS/ASTM Basestock Consistency Study data has been completed. An experimental design for the engine test program has been completed. This program together with the publication of NBS evaluated test procedures contributes significantly for developing base oil characterization and monitoring procedures for lubricants world-wide.

- o A cooperative engine test program sponsored by the U.S. Army, NBS, and ASTM has been initiated. Representatives from re-refiners (MORCO, APR, Booth Oil), major oil companies (Exxon, Mobil, Chevron, Amoco, Sun), engine manufactures (GM, Ford, Cummins, International Harvester), and additive companies (Paramins, Amoco, Lubrizol, Edwin Cooper) have participated in an advisory panel to provide input to the program.

Chemical and Biotransformations in Materials Processing and Durability

Subtask 1

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This subtask is concerned with the role of chemical and biological processes in materials processing and performance. Interdisciplinary expertise in inorganic chemistry and microbiology is used to investigate both processing and durability of materials, providing a basis to develop strategies for controlling materials performance, selecting better materials and predicting environmental consequences of materials use. Chemical speciation of molecular degradation products or process intermediates is often required at typically low service environment concentrations. In many cases, these products or molecules contain metals. Therefore, development and refinement of ultratrace metal speciation methods is a continuing activity in this subtask. Such measurement capabilities, coupled with interdisciplinary materials science expertise have attracted a variety of OA research support and industrial, governmental, and academic guest workers directed toward investigating materials problems requiring advanced scientific concepts and measurements.

Molecular Characterization of Organometallic Polymers: Navy Mil-Spec. Growth of marine organisms (fouling) on ship hulls cost the U.S. Navy \$225 million in 1981. New anti-fouling paints based on copolymers of tributyltin methacrylate, functioning as controlled-release agents, are expected to save the Navy essentially the entire sum mentioned. It is anticipated that Navy requirements in 1986 will be 100,000 pounds or more of organometallic copolymer. Laboratory syntheses must therefore be translated into commercial practice on a relatively short time scale. Characterization of the organometallic copolymers by conventional methods of polymer chemistry has not been satisfactory, and a joint program with the David Taylor Naval Ship Research and Development Center (DTNSRDC) is being pursued to develop a new measurement techniques and provide bases for a Mil-Spec, based on molecular characterization methods, that can be used by the Navy to assure their procurement of acceptable materials. The polymers of particular interest are copolymers of methyl methacrylate (MMA) and tributyltin methacrylate (TBTM).

Much of the Navy's development work has been done on a polymer prepared by the copolymerization of MMA with TBTM under conditions of free radical initiation. Field tests of this material incorporated into antifouling paints on ships have shown 100 percent effectiveness over a four year trial period. A new process has been proposed to the Navy for commercial preparation of the large quantities of polymer needed at a reduced cost. The proposed process involves the preparation of a "prepolymer" of MMA and methacrylic acid (MAA), followed by esterification of the pendant acid residues with tributyltin oxide (TBT0) to prepare the final product. The new process has important cost advantages and offers the promise of better control of polymer properties. However, it is clearly impossible to do the four years of field testing that would be desired before acceptance of a product prepared in a different way. It was possible to make direct comparison of batches of polymer prepared by each of these methods in order to provide the Navy with a quantitative methodology for making the necessary decision as to acceptability of the polymer prepared in the new way.

The molecular characterization methods developed here have relied primarily on the complementary techniques of size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR). While both methods allow quantitation of total tin, only SEC provides information about molecular weight (MW), molecular weight distribution (MWD) and polydispersity; only NMR provides configurational information such as tacticity and distribution of monomer units along the polymer chain.

Processing an OMP for desirable physical attributes requires tailoring the macromolecule to size specifications governing viscosity and mobility. It is even more important to incorporate the tin-bearing moieties in high proportions on the polymer chain in order to gain control over the kinetics of controlled release of the toxic tin-bearing species. Figures 1a and 1b provide this type of molecular information in the case, first, of a copolymer of MMA and TBTM (synthesized by DTNSRDC); and, second, a product having comparable molecular properties that was synthesized by the new commercial process. The weight and number average molecular weight, polydispersity, conversion and transfer of tin from low to high MW species are all comparable (table 1), indicating little or no difference in molecular composition between the commercial product prepared by the new process and the material prepared by copolymerization.

It was discovered and mentioned last year, that a charged tin-bearing species is absorbed on μ -Styragel during the chromatography of OMPs. Desorption by small amounts of injected organic acid permits total recovery of the species. It was found, however, that this step also reactivates the packing surface; when the OMP is injected after reactivation, the electron-rich aromatic centers cleave organotin species from the polymer. Preinjection of a smaller tin-bearing molecule such as tributyltin methacrylate (TBTM) deactivates the packing. The latter stratagem was employed prior to the successful chromatography depicted in figures 1a and 1b.

Complex involving electron-rich centers and organotin compounds have been reported elsewhere. We have not encountered in the literature the ligand displacement mechanism that would explain our chromatographic observations.

As indicated in last year's report, NMR of protons has not been particularly useful, even though protons are the most sensitive nuclei in NMR. At the highest field we have available to us, 9.4 T (400 MHz), the proton spectrum shows much overlap of signals from different parts of the molecule. Carbon-13 NMR has been most useful. In a copolymer made from two vinyl monomers, the major utility of NMR is to provide, after gross compositional information, structural data in the form of "configurational sequencing." If both tacticity and composition are considered, then even at the triad level it is possible to have 20 different sequences with different NMR signals. Because of overlap, it has not generally been possible to see all 20 signals in the polymers under study. Since signals from different groups are well separated, it has been possible to get information of different kinds by study of different parts of the spectrum.

Signals in the β -methyl region of the spectrum (15 to 21 ppm) are relatively insensitive to composition, and reflect only the influence of tacticity as shown in figure 2. Signals in the region of the quaternary carbon (44 to 45 ppm), on the other hand, are insensitive to tacticity and reflect only the effect of composition. "Composition" as used here refers not to overall composition, but to compositional sequencing (i.e., whether alternating, random, or blocky in composition). Finally, the carbonyl region of the spectrum (177 to 181 ppm) is affected by both tacticity and composition and is therefore the most complex as shown in figure 3. NMR spectra of the final copolymer of TBTM and MMA show many interferences from the butyl groups and are difficult to interpret for this reason. It has proved possible, by hydrolyzing with HCl and extracting with chloroform, to remove the tributyltin fragment from the polymer without appreciable loss of methyl groups, and thus to get a material which not only has a simpler NMR spectrum but also is suitable for direct comparison with the prepolymer of MMA-MAA. Tin-119 NMR spectra are similar to spectra of the quaternary carbon region in that they are sensitive primarily to composition and are little affected by tacticity.

A comparison of samples of organometallic polymers prepared both by the Navy process of copolymerization of MMA-TBTM and by the proposed commercial process of esterification of prepolymer by TBTM was made. Consistent with the findings from SEC discussed above, the NMR spectra of both of these materials are essentially the same. If there are differences in the final product, they can only be of a kind which does not strongly affect either tacticity or composition. The polymers show a tacticity which is about 2/3 syndiotactic and 1/3 heterotactic. Only about one percent of the signal arises from isotactic groupings. Compositional information from NMR indicates that the distribution of different monomer units along the chain is random.

Molecular Characterization of Organometallic Polymers: Predicting Field Performance. A novel method for the protection of wood pilings in the marine environment has been developed for the U.S. Navy. This involves copolymerization of two or more monomeric species, typically esters of methacrylic acid--e.g., methylmethacrylate (MMA) or glycidylmethacrylate (GMA) and tributyltin methacrylate (TBTM)--within the wood piling. Co-polymerization appears to occur in situ.

Service life and environmental impact of the preservation treatment are of concern. At the request of the Naval Civil Engineering Laboratory (NCEL), a project was initiated to investigate the chemistry of reactions that occur in wood pilings, speciation of toxic moieties released into the environment, probable effect on non-target marine organisms, and duration of effectiveness.

The controlled release of toxic species depends on many factors such as: the extent of polymerization in situ; the nature of surface reactions between wood components and the tin-bearing moieties; and the chemical reactions involved in transferring the tin species from the wood-polymer matrix into the aqueous environment. Two types of pilings were studied. One had been impregnated with TBTM and MMA (piling no. 3-1), and the other with TBTM and GMA (piling no. 4-5).

In FY83, NBS developed methods for the measurement of total tin released from OMP impregnated wood pilings into artificial seawater. The tin compounds present in the seawater were speciated by coupled high pressure liquid chromatography-graphite furnace atomic absorption spectrophotometry (HPLC-GFAA). Size exclusion chromatography (SEC) was employed to characterize of the molecular properties of tetrahydrofuran (THF) extractable components of the material impregnating the wood. In conjunction with the HPLC-GFAA analyses, a method was developed to significantly enhance the GFAA signal by the addition of selected transition metal salts to the sample. The added transition metal compound is believed to couple with the analyte species, forming a more refractory compound that is less susceptible to loss of volatile species during pre-atomization. Signal enhancements of two to five times or greater, have been observed. This enhanced sensitivity permits earlier detection of organotin release from the wood pilings.

Figure 4a illustrates speciation of the tributyltin compounds present in aqueous solution (artificial seawater) approximately 30 days after immersion of the test specimen. The primary species present, in amounts ≥ 95 percent of the total butyltin present, is the desired, toxic, tributyltin species. The small amount of dibutyltin seen, three to five percent of the total butyltin detected, has important implications. It may be due to impurity or chemical degradation of the OMP materials. However, in view of the large population ($\sim 10^6$ to 10^7 cells/ml) of tin-resistant bacteria that developed during the experiment, the dibutyltin may be the result of bacterial degradation of the tributyltin released by the piling. Further investigations are planned to assess the processing capability of the tin-resistant microbial population.

Evaluation of the OMP as formed in situ is very difficult, as extraction may not remove a completely representative portion of all molecular weight ranges present and conventional acid dissolution for determining total tin destroys the speciation information necessary to assess toxicity.

Figure 4b shows size exclusion chromatograms of THF extractable components of the OMP impregnating the wood pilings prior to immersion. This analysis provides data for comparison of the macromolecular tin-bearing species in the wood in the two different impregnated pilings.

Figure 4c indicates the concentrations of total tin released by a piling into artificial seawater versus time. Although the plots of release for both test specimens appear similar, the rate of release was different, with piling 3-1 (TBTM+MMA) releasing 1.18 ug/cm²/day of tin and piling 4-5 (TBTM+GMA) releasing 0.31 ug/cm²/day. Polymer 4-5 is believed to be cross-loaded whenever polymer 3-1, is not which may account for differences in the release rates.

This combination of HPLC-GFAA is unique in providing data related both to processing in situ and performance under service conditions.

Degradation and Processing of Materials

A long-term project supported by the Office of Naval Research (ONR) concerns the mechanism of the anaerobic corrosion of iron by sulfate-reducing bacteria, postulated to be caused by the removal of hydrogen from the surface of iron (1) by the bacteria, (2) by iron sulfide, or (3) by bacterial removal of hydrogen from iron sulfide. However, control strategies based on these concepts are ineffective.

Results indicate, however, a novel mechanism for the anaerobic corrosion of iron. Severe anaerobic corrosion occurs in the absence of both direct bacterial contact and iron sulfide. The agent causing corrosion is a volatile, highly-reactive phosphorus-containing compound, produced by the sulfate-reducing bacteria, which reacts with iron to form iron phosphide as a corrosion product. A similar compound is produced by the reaction of hydrogen sulfide and hypophosphite (PO₂), phosphite and phosphate. Identification of this volatile compound by mass spectrometry is in progress. Based on these findings it is suggested that any organism that produces hydrogen sulfide, under anaerobic conditions, in the presence of inorganic phosphorus compounds should stimulate the corrosion of iron, providing the iron does not have a film of iron sulfide. The presence of soluble iron (Fe⁺⁺) in the vicinity of the bulk iron inhibits film formation and permits corrosion by the P-compound.

Acidification of the corrosion product yields phosphine which can be detected by gas chromatography employing a flame photometric detector (fig. 5). Consequently, this procedure appears to be a highly useful diagnostic test for establishing biological corrosion in the field and will be evaluated in field trials on buried gas pipelines in West Virginia,

suspected to have failed because of bacterial anaerobic corrosion. The Department of Transportation has appointed a guest worker to investigate bacterial corrosion within this subtask. One purpose of the program is to develop field tests and equipment to accurately predict the location where sulfate-reducing bacteria are actively causing corrosion on underground steel pipelines. A second aim is to develop better tests for accurately determining if corrosion on an exposed pipeline is bacterial. The Tennessee Gas Transmission Co. and the West Virginia Public Service Commission have agreed to assist NBS in field testing.

In addition to hydrogen sulfide and volatile P-compound production by sulfate-reducing bacteria, methylmercaptan and dimethylsulfide were also identified as metabolic products (fig. 6). The relative amounts of H_2S and methylmercaptan produced varied, depending on the composition of the growth medium. These two organosulfur compounds were found to be relatively non-corrosive to iron under anaerobic conditions, however.

Very recent preliminary observations have indicated that the volatile P-compound may also be produced in large quantities in a highly metal-contaminated sediment of the Schwarzbach, West Germany. This river flows into the Ginsheimer Altrhein, near the junction of the Main and Rhein rivers at Ginsheim. It drains a highly industrialized area and may forecast the type of natural environment where biogenesis of the novel corrosive phosphorus compound and resulting severe iron corrosion could occur in this country.

The biocorrosion investigations, as well as other work on chemical and biological transformations of bulk materials, increasingly demand rapid surface analytical techniques for characterizing microorganism distributions and chemical transformations. Consequently, the novel development of epifluorescence microscopy techniques for surface mapping of materials transformations represents a valuable, non-destructive, real-time measurement advance. This technique can now be used to examine fluorescent materials distribution on surfaces. A laboratory computer was coupled to a camera mounted on an epifluorescence microscope to analyze the distribution of iron-corroding bacteria stained with a fluorescent dye. A computer picture was drawn depicting distribution of the organisms in a microscope field (fig. 7). This technique should also be adaptable to analysis of chemical species on materials surfaces through the use of chemical species-selective fluorescent dyes. Such a technique would be especially promising in rapid, real-time non-destructive analysis of materials surfaces, and is the subject of a proposal to the NBS Office of Non-Destructive Evaluation.

Epifluorescence mapping was also applied to Paint Research Institute (PRI) sponsored work to study the defacement of paint films by algae and bacteria (organisms that are not necessarily controlled by mildewcides incorporated into paints). It was found that algae were responsible for paint film disfigurement on paint samples from Maryland, Oregon, and from an experimental test panel site in Florida. A spherical alga resembling Pleurococcus caused disfigurement on the Florida panels and a filamentous alga was responsible for the disfigurement on the Oregon samples. Several methods were investigated in order to develop an

accelerated testing procedure for algal paint film disfigurement. It was found that pine blocks, painted with an experimental test paint, then dipped into an algal agar medium, supported algal surface growth in testing chambers. The degree and distribution of algal disfigurement was mapped using the epifluorescence microscope equipped with a photometer. Chlorophyll in the algal cells fluoresced red under ultraviolet illumination, and, by scanning the surface of the wood block with the microscope/photometer system, a distribution map of algal growth was obtained (fig. 8). This work will help the PRI in adopting test methods and algal control agents for possible incorporation in paints.

Another measurement advance was made in the area of environmental organometal detection and speciation. The previously described purge and trap flame photometric gas chromatography technique (P/T-GC-FPD) for tin species detection has been extended by coupling a flameless atomic absorption (AA) detector specific for mercury to the FPD gas exit port for tandem detection of tin and mercury species (fig. 9). This new P/T-GC-FPD-AA offers an attractive new method for aqueous mercury species determination but, most importantly, this system is useful in studying environmental situations where transmethylation reactions may dictate the levels of toxic tin and mercury species. Earlier work in this group suggested that a tin-mercury transmethylation was possible and should be considered as a potentially significant route to environmental methylation of certain metals. In collaboration with colleagues of Michigan State University, assistance is being given to the State of Michigan in the examination of sediments from a Michigan lake subjected to tin and mercury pollution. The P/T-GC-FPD-AA technique is being applied to measure mercury and tin species levels for developing an understanding of the role of potential tin-mercury interactions dictating levels of toxic species. Methyltin species and inorganic mercury have been detected at several sites in and near the lake. A chromatogram of one of the samples is shown in figure 9.

Processing Mechanisms and Metals Biorecovery

Biotechnology holds promise for greater efficiency in synthesis and utilization of critical materials and is currently under intensive study at NBS. Unfortunately, virtually no fundamental understanding of rate-limiting factors and mechanisms of metals bioprocessing, and of possible process measurement systems are available to realize this potential and solve pressing needs for recovery or extraction of critical metals. In the past year, requests have been made for generation of fundamental programs aimed at solving these measurement problems by several outside agencies including DOD, DOI, and the Electric Power Research Institute.

Global, economically critical resource management of strategic metals increasingly will rely on novel, efficient means for their production and conservation. Working in collaboration with colleagues at the University of Cincinnati, it was discovered that strategic and toxic metals were dissolved from sediments and authentic metal sulfides by a common biogenic metabolite, methyl iodide (tables 2, 3).

In the case of metal sulfides, volatile and diagnostic methylsulfur compounds were also detected (table 4) by flame photometric gas chromatography analysis of vapors above methyl iodide--metal sulfide mixtures. NMR was used to follow the kinetics of methyl iodide-sulfide reactions, and to identify reaction intermediates (fig. 10a, b, c). With a sodium sulfide-methyl iodide mixture, dimethylsulfide was shown to be an intermediate, eventually reacting with additional methyl iodide to form trimethylsulfonium ion (fig. 10b). The rate constant for the methyl iodide-sodium sulfide reaction was approximately $3 \times 10^{-4} \text{M}^{-1} \text{s}^{-1}$. Heterogeneous reactions with CH_3I and PbS and SnS also showed dimethylsulfide and trimethylsulfonium ion. In the case of SnS , production of a methyltin species was indicated by the chemical shift of a small peak upfield from trimethylsulfonium ion. Confirmation of the methyltin species was made by flame photometric gas chromatography. This work represents the first characterization of methyl iodide-metal sulfide reactions, and is a novel application of NMR to directly study reactions between solids and liquids at environmental levels in aqueous solutions. This work also shows that the mechanism of metal sulfide solubilization by methyl iodide is consistent with the theory of S_N^2 nucleophilic substitution reactions. Furthermore, this work suggests that small biogenic metabolites could be involved in the as yet unknown mechanism of metal sulfide solubilization by Thiobacillus. Methyl iodide itself may be useful in metal ore leaching and processing.

In last year's report work was described involving the first demonstration of a heavy metal detoxifying enzyme system in iron- and sulfur-oxidizing Thiobacillus ferrooxidans--an organism contributing up to 25 percent of U.S. copper production and considered as a leading candidate for use in coal biodesulfurization processing. This work has been extended by investigating toxic metal resistance in heterotrophic (carbon consuming), acidophilic organisms which are intimately associated with Thiobacillus in metal processing, but for which little information is available on their effects on the rate of metals dissolution. Using a gas chromatography-atomic absorption system, it was found that these heterotrophic organisms also detoxify mercuric ions ($\text{Hg}^{2+} \rightarrow \text{Hg}^0$), which are regarded as possible rate-limiting toxicants in bioprocessing of certain coals and metal ores, at higher concentrations than Thiobacillus can tolerate, and thus may allow metal dissolution by Thiobacillus in an otherwise toxic environment. This is the first report of metals processing by these heterotrophic organisms. It is possible that genetic exchange between these organisms and Thiobacilli may also occur, conferring toxic metal resistance or other properties. As a first step along these lines, collaboration has once again begun with molecular geneticists at Washington University, St. Louis, to characterize the heterotrophic mercuric reductase enzyme and to compare it with the rather unusual Thiobacillus reductase. It is now known that the heterotrophs contain plasmid (extrachromosomal) DNA. Almost invariably, mercury resistance is plasmid coded, and defining plasmid markers for metal resistance would be a useful first step toward eventual technological genetic improvements in these organisms.

Bioprocessing of metals increasingly involves not only solubilization of metal ores, but also biorecovery processes where organisms are used to precipitate or adsorb metals in process streams. Small angle neutron

scattering (SANS) was investigated as a new technique for measuring rates of metal particulation in metal-depositing organisms, and how these rates may be altered by cultural manipulations. SANS cannot replace electron microscopy for qualitative examination of specimens for metal uptake, however, it offers promise as a new non-destructive measurement technique for real-time measurements of metal uptake rates in populations of organisms. The model systems being used are pure cultures of magnetite-depositing bacteria (in collaboration with microbiologists at the University of New Hampshire), and uranium depositing microorganisms obtained from colleagues at Oak Ridge National Laboratory. Preliminary experiments using the NBS SANS facility have established quantities of organisms needed and optimal suspending media for best signal-to-noise ratios. Differences in scattering between organisms exposed to uranium and those not exposed were noted (fig. 11A), likely due to uranium uptake, confirmed by transmission electron microscopy with energy dispersive X-ray microanalysis (TEM-EDAX) (fig. 11B). Additional experiments are planned to generate information on rate of formation and size distribution of metal particles in cells. The uptake of metals on cells by TEM/EDAX was measured by direct examination of cells placed on grids without conventional dehydration and fixation procedures. These procedures usually involve alcohol dehydrations which can remove lipophilic organometallic compounds from cell envelopes. Uptake of organolead and organotin compounds by *Pseudomonas* 244 was shown by TEM-EDAX spectra on whole cells adsorbed to carbon films on nylon or copper grids (fig. 12). This demonstration of direct electron microscopy now permits measurement of organometal uptake in planktonic and adsorbed cells in metal bioprocess streams. Strong collaborative support from Division personnel expert in SANS and TEM-EDAX supported these investigations.

Chemical Factors in Tribology

Subtask 2

Recycled Oil Performance

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Current technical effort in this subtask is directed towards better understanding of the mechanisms of friction and wear and the chemical factors that affect these mechanisms. At the same time, the subtask provides, within the Center for Materials Science, major scientific and technical competences in chemical stability of complex organic mixtures at metal and ceramic surfaces, chemical reaction kinetics in complex condensed-phase systems, friction and wear of materials, tribology, and detailed chemical characterization of complex organic molecules such as lubricants and fuels.

In addition, this subtask has the special assignment of providing a technical base of data and measurement methodology to support the Bureau's work on recycled oils. This task is mandated by Congress, under the Energy Policy and Conservation Act, to provide test procedures which can be used to establish the substantial equivalency of virgin and recycled oil products.

Efforts in recycled oil have been concentrated in three areas: (1) Laboratory bench performance tests have been developed which can correlate to engine test results. (2) The NBS/ASTM Basestock Consistency Study data has been published and analyzed to provide the most comprehensive data base on lubricating base oil composition to date. (3) An Army/NBS/industry engine test program is being conducted to validate test procedures previously recommended by NBS for automotive lubricating base oils.

The combined information from these three areas will provide a significant contribution to understanding the chemical and physical parameters which affect the oxidation and tribological performance of a lubricating oil.

Tribological Properties of Ceramics

Friction and wear test capabilities have been expanded to include evaluation of ceramic materials. Current capabilities include measurement of friction and wear of ceramics at speeds of up to four meters per/second sliding speed, stresses in excess of 20,000 kg/cm² (284,000 psi), and bulk temperatures up to 500 °C. A second apparatus is being modified to increase the temperature limit to 1000 °C. A third apparatus is being designed to operate at up to 1500 °C. This would allow tribological evaluation of advanced ceramics for high temperature applications such as the adiabatic diesel engine. Various high temperature lubrications systems such as vapor phase deposition and solid lubrication are also being investigated.

A theoretical model is being developed for calculating contact junction temperatures for wearing contacts in a four ball wear tester. This model uses various material parameters and test conditions to predict mean contact junction temperatures over a wide range of speed and load.

Hydrocarbon Characterization

The Energy Conservation and Utilization Technology Program (ECUT) of the Department of Energy has requested the Division to isolate and characterize complex hydrocarbon mixture, such as lubricating base oil, into compound classes in order to identify the compound class which has different frictional characteristics and oxidation stability.

Liquid chromatography methods have been developed to separate three lubricating base oils into molecular compound classes and performance characteristics data indicate that there are wide variations in antioxidant capacity and friction and wear properties for different molecular compound classes derived from the separation scheme.

The separation scheme is shown in figure 13. The process has three steps. The base oil is separated on a clay column, generating a saturate/aromatic hydrocarbon fraction and a polar fraction. The saturate/aromatic fraction is then separated into individual saturates and aromatics fraction on a dual packed, alumina/silica gel column. The polar fraction is separated further on neutral alumina adsorbent to obtain subfractions, such as polynuclear aromatic compounds, basic nitrogen compound, esters, and carboxylic acid type of compounds. Each major fraction and compound class of polar subfractions is characterized chemically by analytical methods such as infrared, high resolution mass spectrometry, gel permeation chromatography, and C^{13} NMR. In addition to these analytical methods, performance tests are performed. They include antioxidant capacity titration method to determine oxidation stability of the fractions, and sequential micro sample wear tests, to determine the friction and wear characteristics of these molecular compounds.

The polar fraction of the base oil has both oxidation stability and low friction in comparison to the base oil. On further separation of the polar fraction, the four polar subfractions again possess different oxidation stability and frictional properties. The acidic fraction of a 600N base oil was found to have a coefficient of friction only half of that of the other constituents of the polar fraction (0.04 vs 0.08). This result is significant towards the goals of the ECUT program--more efficient energy conversion and utilization by the control of friction and wear. This finding has led to a cooperative research program with several major oil companies to develop methods to isolate and identify the molecular structures responsible for such low friction characteristics from the extract phase of the base oil solvent extraction refining process.

Friction and Wear Test Methodology

Under the ECUT program, a new test methodology for friction measurement has been developed for the various compound classes separated from three lubricating base oils of different viscosities. In this procedure, a pure paraffin is used to provide the wear-in. After one hour, the wear scar diameter is 0.67 ± 0.02 mm. The relative surface roughness is two micrometers. The sample is then introduced, and the load is increased step-wise every five minutes to determine the effective range (speed/load). Within the effective range, an entirely new run is made. After one hour of wear-in process, the same sample is introduced under constant condition friction test for ten minutes. Usually a constant friction level is found as shown in the curve A of figure 14 in comparison to a normal run without the wear-in process (Curve B of figure 13). This friction trace is then the true friction of the lubricant. The sample for this friction curve is a polar subfraction of the 150N base oil.

The effective load region of the three major fractions, are 15 to 20 kg (saturates); 25 to 35 kg (aromatics) and 45 to 50 kg (polars). The constant condition test results indicated that the polars give low coefficient of friction (0.078 to 0.085) at higher loads. The polar fraction is separated further into four subfractions and are evaluated with the same

wear test. The effective load regions of the polar subfractions are very similar. However the plots for the friction traces show distinctly different characteristic shape for each subfraction. Coefficient of Friction (COF) values for the subfractions were low (0.061 to 0.085) with the exception of the P-6 subfraction of the 150N base oil which has a COF of 0.105.

The Constant Condition Tests (CCT) of the polar subfractions yield very interesting data. At CCT, the P-6 subfraction of the 600N base oil gave a much lower coefficient of friction, which amounted to about half of all other subfractions, and also produces the lowest wear scars of all the subfractions. Therefore, the 600N P-6 subfraction needs to be further separated and studied.

In summary, the polar fraction was found to provide low friction at higher loads. The polar subfractions yielded striking different coefficient of friction within the effective regions. Specifically, the P-6 subfraction of 600N base oil produced a coefficient of friction approximately half that of the other subfractions.

The present size exclusion-graphite furnace atomic absorption apparatus has been expanded to include an ultraviolet (UV) detector to enhance speciation capabilities of UV sensitive chromophores. High molecular weight iron containing organometallic species generated in a wearing contact junction were found to absorb in the UV region at 254 nm. The UV detector has proven much more sensitive at detecting these organometallic compounds than the previous refractive index detector. Analysis of used engine oils has shown that these same high molecular weight organometallic species are formed in an operating engine.

Standard Reference Material (SRM) Production--Chlorine in Rerefined Oil

The Environmental Protection Agency (EPA) is in the process of issuing regulation on hazardous waste. One of the items is used oil and its polychlorinated bi-phenyls (PCB) content. It is widely anticipated that the limit on polychlorinated biphenyls (PCBs) in oils will be 50 ppm, and the proposed regulation will take effect in the Fall of 1983. When this regulation takes effect, the demand for PCB or chlorine analyses in various oils will soar. One of the key problems in this area is the lack of standard reference materials for test calibration. There are currently many tests available and results from one test differ widely from another.

In conjunction with the Office of Standard Reference Materials, we are issuing a chlorine in oil standard to help resolve this critical environmental concern. This standard was developed after several years of sampling different rerefiners products and developing a data base from five different analytical procedures for chlorine analysis including, neutron activation analysis, x-ray fluorescence, microcoulometry, ASTM D1317 sodium alcoholate method and ASTM D808 oxygen bomb method. Of these methods x-ray fluorescence and neutron activation analysis have been selected to certify chlorine values. This standard is scheduled for release during the Fall of 1983.

Analysis for a second SRM (Sulfur in Virgin Base Oil) has also been initiated. The effect of sulfur on oxidation stability and increasing use of mixed crude feedstocks in refining have generated a need for standards containing low sulfur concentrations in oil matrices. Sulfur analyses of oils from our study on recycled oils have pinpointed a number of oils over a range of values. Since there are currently no available standards for low sulfur concentrations in oil matrices, we are currently engaged in certifying five oils for sulfur. This project will be completed in the Spring of 1984.

Standard Reference Material Research

During the past year, two novel separation schemes for the complex hydrocarbon mixtures were developed. These separations have permitted us to isolate narrow molecular weight compound classes. Although it was shown that gravity flow liquid chromatograph provided good separation, preparative high pressure liquid chromatography provided the same quality results in one-tenth of the time. Initial results from stability and wear tests uncovered a whole host of interesting petroleum fractions. Some fractions contain high antioxidant values while still others have low frictional values.

However, the interesting fractions only compose one to two percent of the entire material. This makes efforts to produce SRM material difficult. Most of these compound types have been previously extracted during the refining processes. We have now arranged with two oil companies to send the extract containing 40 percent of the material to NBS.

On a cooperative study between NBS, Southwest Research Institute and Bartlesville Energy and Technology Center we are performing stability studies on synfuels in various stages of processing. Efforts will be made to parallel the petroleum research by separating synfuels into various fractions and studying relative effects on stability and gum formation tendencies.

SRM research in FY83 led to two proposals for working capital funds for FY84. These include sulfur in high molecular weight (C_{18} to C_{44}) petroleum fractions and chlorine in re-refined oils. These projects have been accepted by OSRM. The feasibility of providing a standard for low nitrogen levels in complex hydrocarbons is also being investigated.

Lubricant Performance Bench Tests

A Thin Film Oxygen Uptake Test (TFOUT) has been developed to evaluate the oxidation tendencies of automotive engine lubricants. A standard Rotary Bomb Oxidation Test (RBOT) was modified and a procedure was developed using a catalyst package to simulate high temperature oxidation products from an automotive engine. A good correlation was found between test results and actual oxidative performance experienced in field studies. The catalyst package that was developed for the TFOUT test has been produced as a standard reference material (SRM 1817). The test procedure is currently under round robin testing in ASTM as a standard test method for evaluation of the oxidation stability of automotive lubricants.

A cooperative effort between NBS and 11 companies was formed to relate the chemical composition of lubricating base oils to oxidation tendencies. In the cooperative program, nine companies sent over 100 base oils to NBS with associated analytical data. These virgin oils from various crude sources and processing technologies were tested in the TFOUT and the results correlated with the composition parameters. New insights were gained from the various functional dependencies of the parameters. The amounts of saturates and sulfur compounds were shown to have the major influence on the base oil response to additives.

In addition, 14 selected base oils were blended with six different detergent/inhibitor additive packages and evaluated using the TFOUT test. Results indicated that additive response is primarily a function of saturate content, sulfur content, and viscosity index of the base oil. Chlorine content and total nitrogen content were also found to affect oxidation stability but to a lesser extent. Data from these two programs are vital for understanding the relationship between base oil compositions and performance. This basic knowledge is important in setting specifications for base oils in general, but crucial in setting specifications for re-refined base oils.

Recycled Oil Program--Basestock Consistency Study

The relationship between chemical composition of base oils and performance is not understood. Current practice calls for constant crude source and processing technology to ensure consistent quality. Each crude source change necessitates a complete engine testing of all products for requalification. Sometimes the products have to be modified and redeveloped. A basic understanding between composition and performance can suggest alternate processing technology to remove undesirable compounds and improve product performance. Although formulated in the context of the Recycled Oil Program, this activity has implications for all areas of the lubricating industry.

The ASTM/NBS Basestock Consistency Study (BCS) involves four virgin oil producers and six re-refined oil producers submitting monthly samples of their regular production basestock for a period of 13 months for test analysis by a group of 14 industrial and government laboratories. In addition, one blind control sample was sent out each month. Fifty-three characteristics were measured on 129 oils. Many tests have multiple data entries and some tests were performed by more than one laboratory. The tests consisted of viscosity and physical property tests, chemical and hydrocarbon type analyses and general performance and oxidation tests.

The data analysis of the Basestock Consistency Study (BCS) was approached along several different avenues. These include computer data compilation, development and application of statistical methodology, and modeling. The primary goals are to: (1) develop methodology or criteria to assess produce consistency; (2) selection of oils for further engine testing; (3) correlation between performance and physical and chemical property data.

The data publication (NBS Special Publication 661) includes 191 data tables, 240 distributional and run sequence plots, plus a complete listing of test methods. The results of this study are being analyzed by statistical methods. This invaluable data base will provide an universal standard for lubricating base oil production quality control world-wide for decades to come. In addition, this data base fills a vacuum in addressing the batch-to-batch quality control for re-refined base oils, a key issue in oil recycling.

Engine Test Program

Industry will only accept engine testing and field performance as the final criteria for automotive engine lubricating oil quality. In addition, for re-refined oil there is a fear of contamination from cutting fluid, electrical transformer oil, hazardous waste, and wear and residual additive metals. The effect of possible contaminants on the re-refining process and engine performance is not well known.

ASTM engine sequence tests have been experimentally designed using statistical analysis and modeling of the BCS data with the NBS developed Thin Film Oxygen Uptake Test (TFOUT). This test has a correlation with ASTM engine sequence IIID test data.

A cooperative engine test program has been initiated. The NBS/Army/industry engine test program will determine a set of test procedures that are capable of measuring base oil consistency. NBS has developed a tentative set of tests and qualifying procedure for lubricating oils [1]. The study will have world-wide impact on the setting of specifications for automotive engine lubricating base oils.

[1] Hsu, S. M., Ku, C. S., and Becker, D. A., Base Oils for Automotive Lubricants SAE SP-526, 87-105, 1982.

Table 1. Molecular Characterization of OMPs by Size Exclusion Chromatography

	Commercial OMP		Navy OMP	
	ΔRI^*	GFAA**	ΔRI^*	GFAA**
M_w (daltons)	63,700	65,000	52,200	41,600
M_n (daltons)	40,900	28,500	32,600	18,500
MWD	1.56	2.28	1.60	2.25
Conversion (%)	95.7	90	96.2	90
Recovery of Sn (%)	---	97.3	---	94.1

*RI (differential refractive index) is mass-sensitive.
 **GFAA (graphite furnace atomic absorption spectrometry) is tin-specific under the conditions selected for this measurement.

Table 2. Release of Metals from Baltimore Harbor Sediments

	Colgate Creek			Jones Falls		
	<u>Pb</u>	<u>Mn</u>	<u>Cu</u>	<u>Pb</u>	<u>Mn</u>	<u>Cu</u>
Sediments/CH ₃ I	1.360	0.365	0.032	1.510	0.029	0.056
Sediments Only	0.460	0.268	0.017	0.770	0.015	0.013

*mgL⁻¹ dissolved metal.

Table 3. Dissolution of Lead from Lead Chalconides*

Contact Time (ks)	PbS	PbS/CH ₃ I	PbSe	PbSe/CH ₃ I	PbTe	PbTe/CH ₃ I
8.24	0.04	0.70	0.05	4.11	0.13	4.47
15.75	0.11	4.91	0.04	4.89	0.07	7.03
77.70	0.51	17.50	0.01	14.50	0.01	15.40

*mgL⁻¹ dissolved lead.

Table 4. Relative Quantities of Released Methylsulfur Compounds from Metal Sulfide (50 mg)--Methyl Iodide (5 μ L) Reactions in Water*

<u>Metal Sulfide</u>	<u>(CH₃)₂S</u>	<u>(CH₃)₂S₂</u>
CaS	3,000,000	50,000
PbS	448,000	110,000
FeS	55,000	---
AsS ₂	14,000	---
SnS ₂	7,700	1,000
HgS (red)	2,400	---

*Numbers represent the integrated chromatographic areas (in arbitrary units) after 96 hr incubation in the dark at 22 °C.

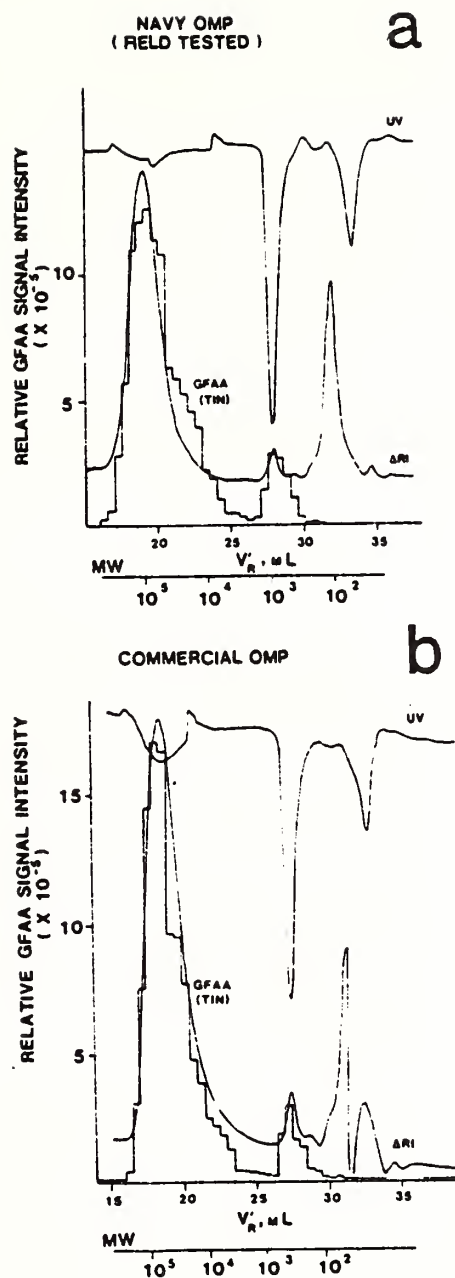


Figure 1 (a) Size exclusion chromatograms of a Navy OMP (OMP-2) and (b) a commercially synthesized OMP (OMP-21 F). Both mass-sensitive RI chromatograms and tin-specific GFAA chromatograms yield a wealth of molecular data: M_w , M_n , MWD, and monomer conversion (the relative proportions of mass or of tin in high- and low-MW fractions). The molecular similarity of the commercial OMP to the successfully tested Navy OMP shows that it is feasible to set criteria for the synthesis of such materials based in part on chromatographic data.

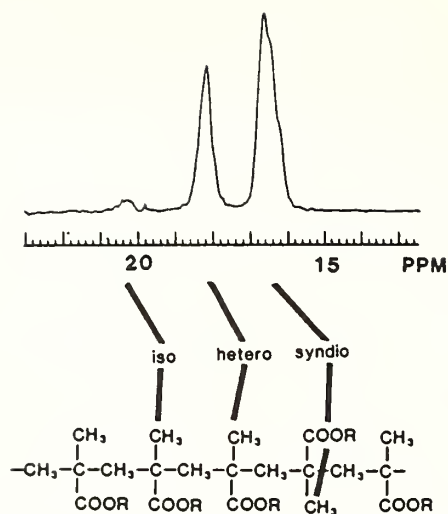


Figure 2 NMR spectrum at 50 Mhz of β -methyl carbons in a 1:1 copolymer of MMA-MAA. The β -methyl signal is split into a triplet by effects of tacticity as diagrammed; note that this triplet is not further split by compositional effects.

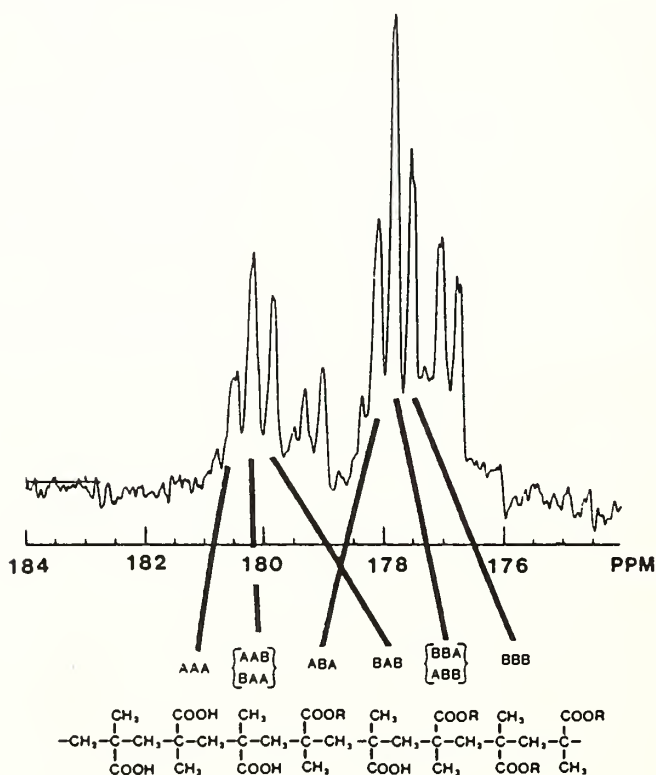
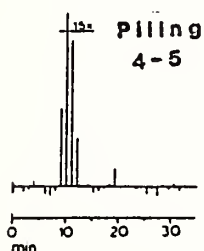
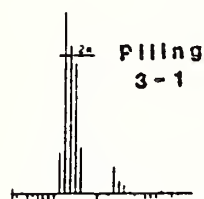
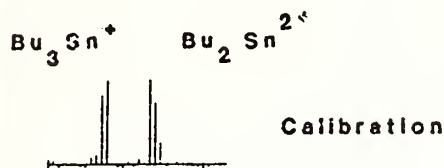
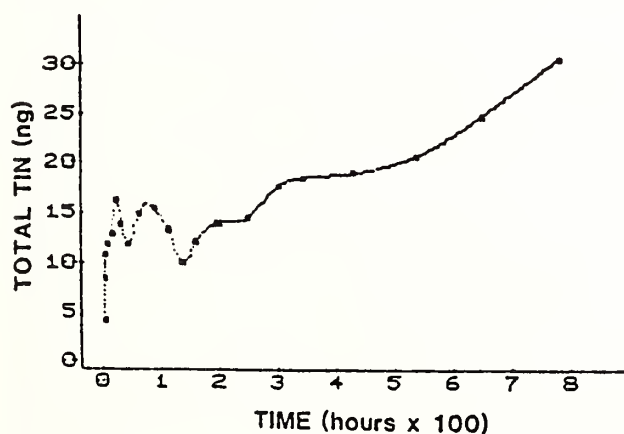


Figure 3 NMR spectrum at 50 Mhz of carbonyl carbons in a 2:1 copolymer of MMA-MAA. The carbonyl signal from each group (COOH or COOR, R = CH₃) is split into a triplet by compositional effects as diagrammed for syndiotactic polymer. The smaller higher field triplet flanking each signal arises from heterotactic groupings; signals from isotactic sequences are too weak to be seen. The additional small splittings on some of the peaks are due to the effect of pentad structures.

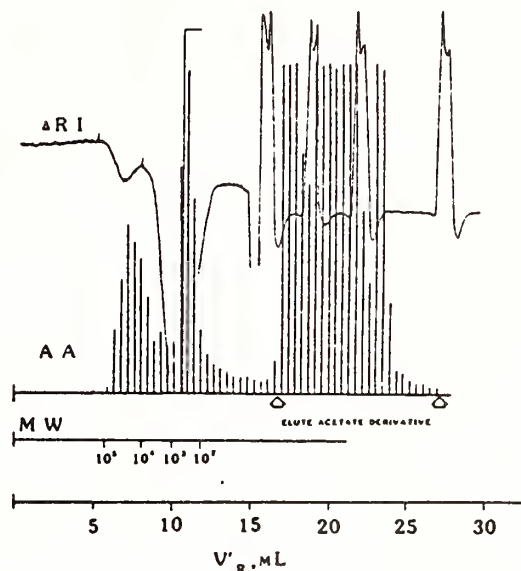
A Cation
Exchange
Chromatography



C PILING RELEASE OF TIN



B SIZE EXCLUSION CHROMATOGRAPHY
THF EXTRACT OF WOOD PILING NO. 3 - 1



THF EXTRACT OF WOOD PILING NO. 4 - 5

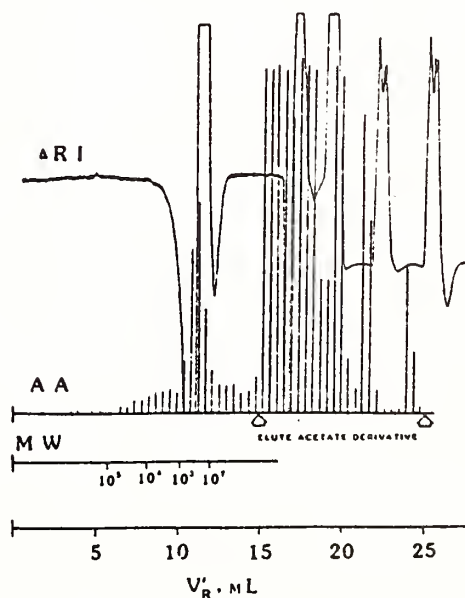


Figure 4 (A) HPLC-GFAA chromatogram showing predominately Bu_3Sn^+ species (95% to 97%) released into aqueous solution by wood pilings. (B) SEC chromatograms showing significant differences in the high molecular weight content of the OMP extractable from the pilings. (C) Plot of total tin released into solution versus time for piling 3-1. Piling 4-5 gave a similar pattern, but at lower tin levels.

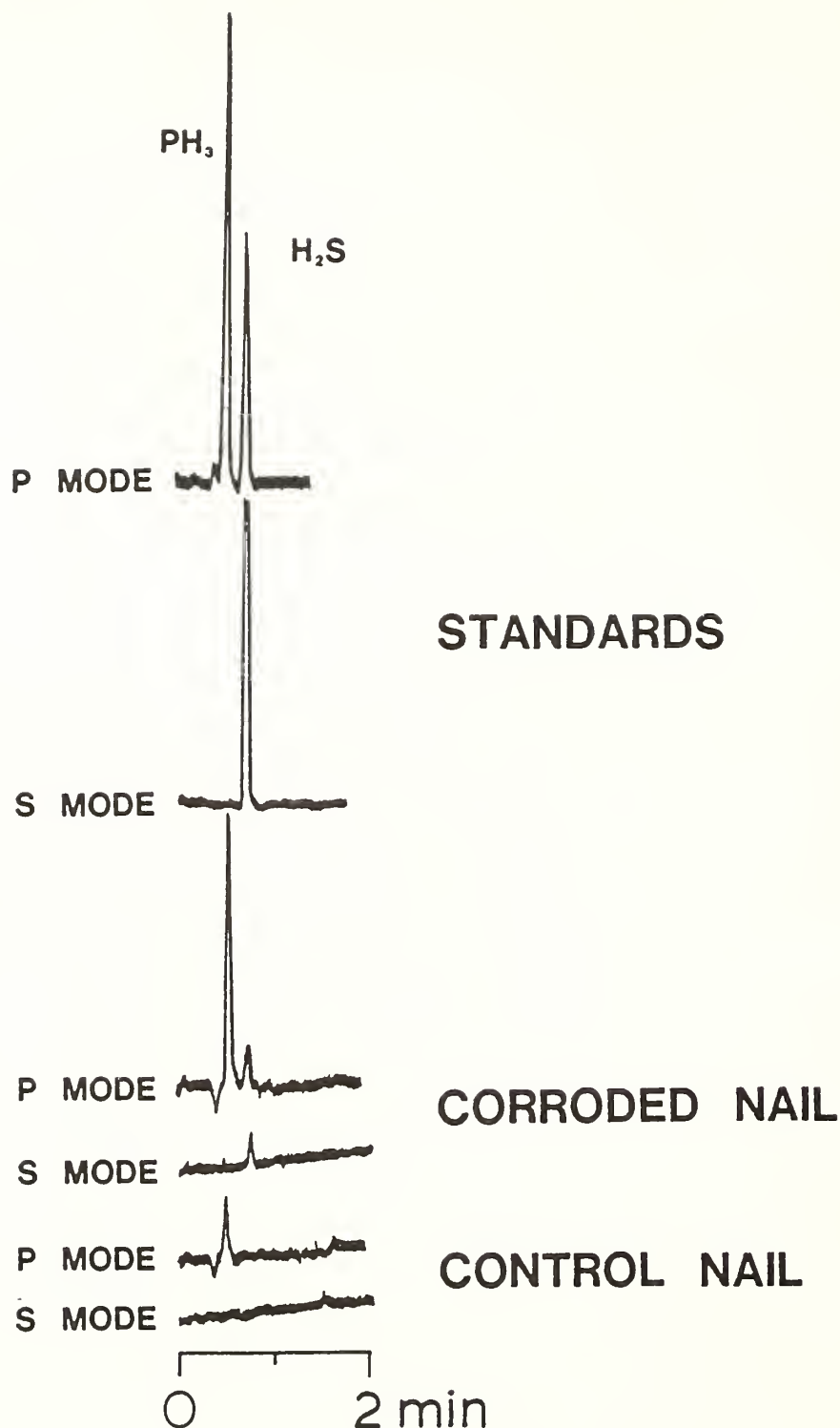


Figure 5 Flame photometric gas chromatography (GC-FPD) detection of reference PH_3 and H_2S in S- and P-selective detection modes. Corrosion products on iron nails, resulting from the action of volatile metabolites from sulfate-reducing bacteria, were acidified with 1:1 H_2SO_4 and the resulting gases were injected on to the gas chromatographic column. Some H_2S and considerable PH_3 were detected. Control nails, not exposed to bacterial gaseous metabolites showed little or no PH_3 and H_2S production.

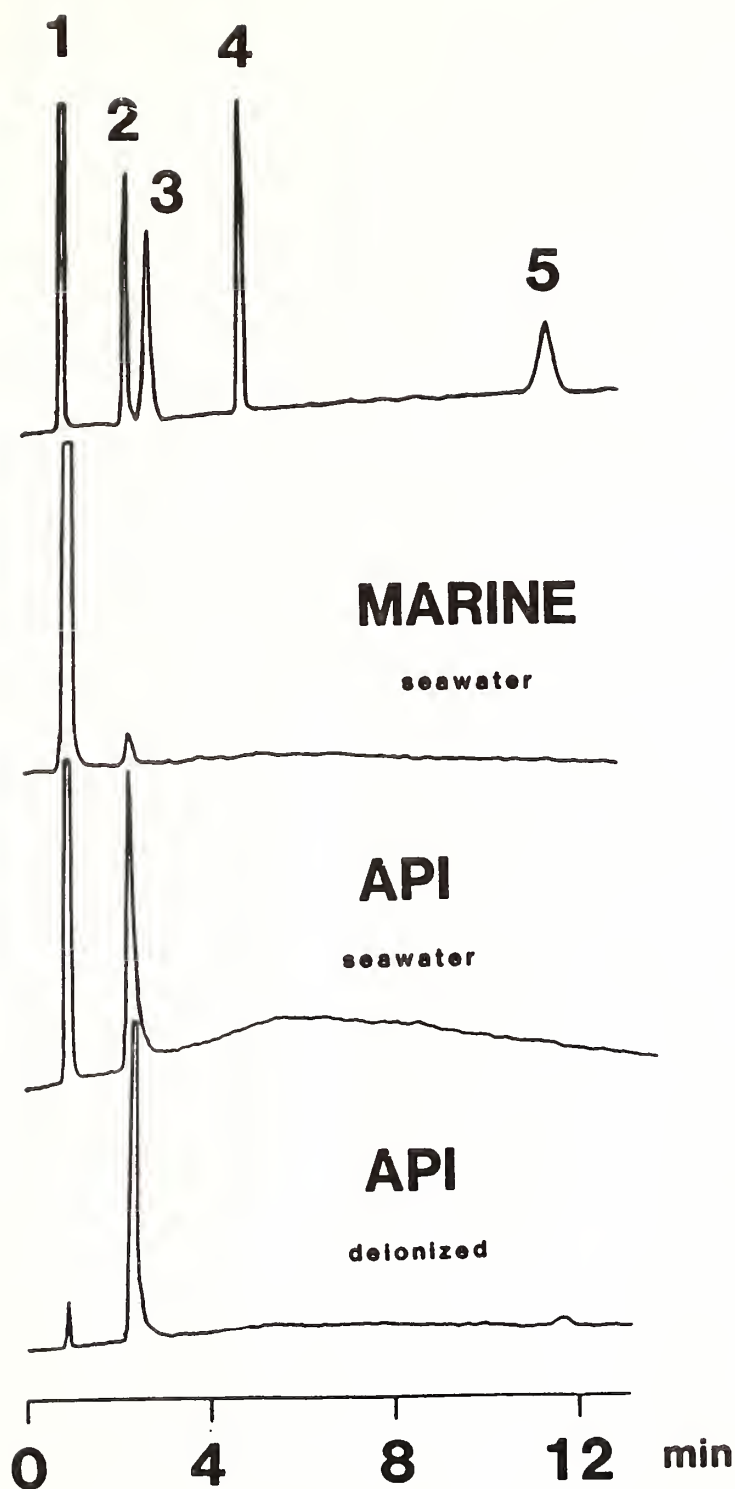
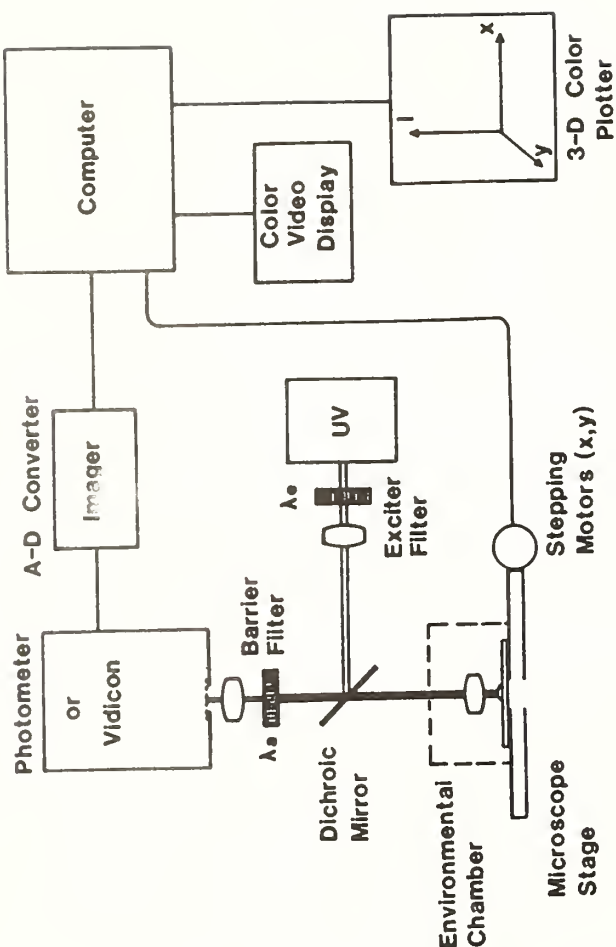


Figure 6 GC-FPD detection of volatile sulfur gases produced during growth of two strains (marine, API) of iron-corroding, sulfate-reducing bacteria on an agar medium made with seawater (sulfate-rich) or deionized water (sulfate-poor). These organisms generate H_2S by respiratory sulfate reduction, however it was discovered that methylmercaptan (CH_3SH) was also produced. In sulfate-poor medium, methylmercaptan and a small amount of dimethyldisulfide were produced, and, as expected, little H_2S was detected. Standards: 1, H_2S ; 2, CH_3SH ; 3, $(\text{CH}_3)_2\text{S}$; 4, CS_2 ; 5, $(\text{CH}_3)_2\text{S}_2$.



Desulfovibrio API Strain

778X Acridine Orange stained

$\lambda_e = 440-490 \text{ nm}$ $\lambda_s \geq 520 \text{ nm}$

Figure 7 Block diagram of epifluorescence microscope imaging (EMI) system. At left, a computer generated map and its inverse (top, left) were generated from a video camera and show the distribution of stained sulfate-reducing bacteria in the microscope field. The cells were stained with a fluorescent dye which, when excited by blue light, emits green light.

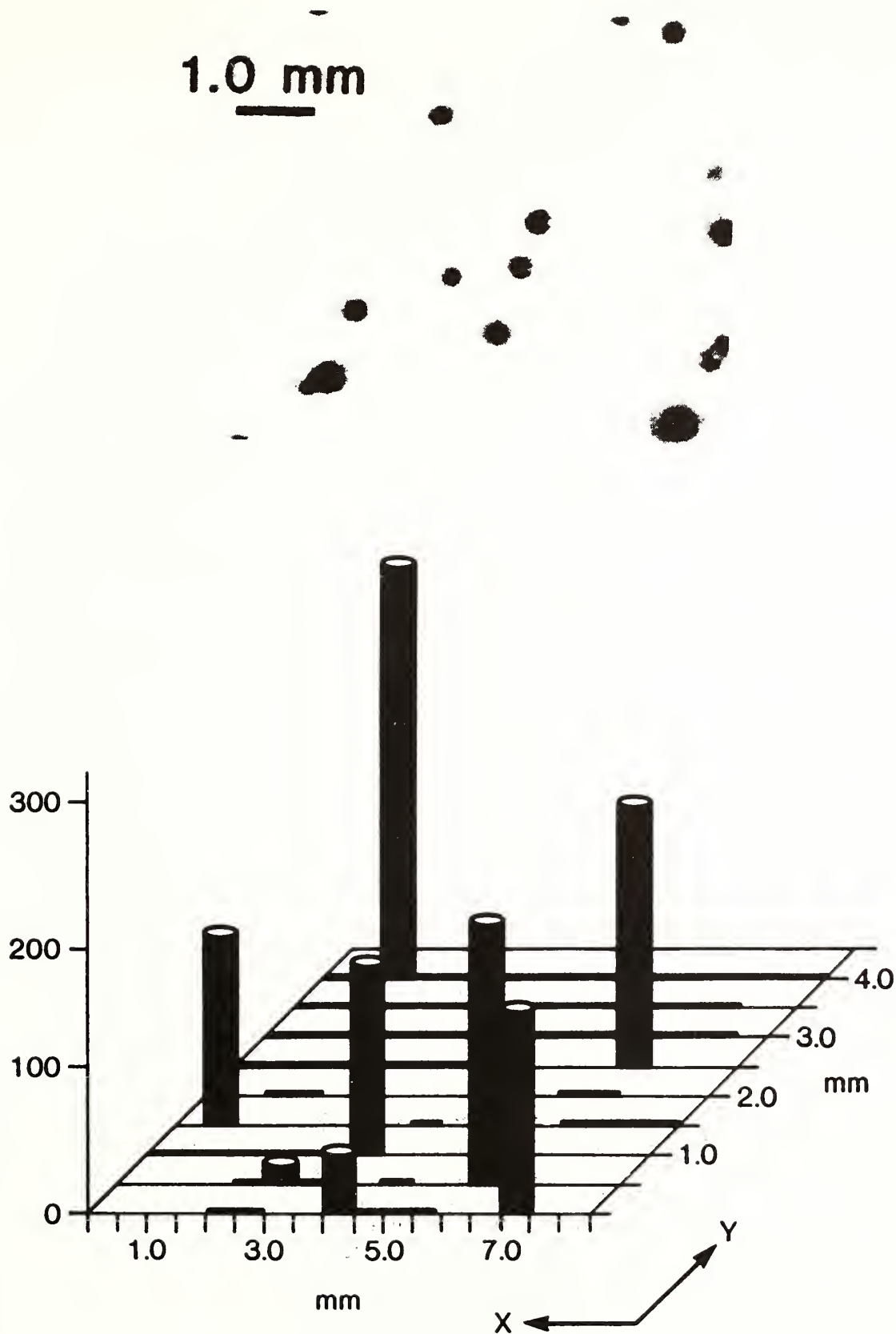


Figure 8 Photograph of algal colonies (top) disfiguring a painted wood test block. The surface of the wood block was scanned with the EMI system using an exciting wavelength of 365 nm. Emitted light from UV-induced chlorophyll fluorescence (red) was quantitated with a photometer, generating a fluorescence intensity map of the surface of the block (bottom).

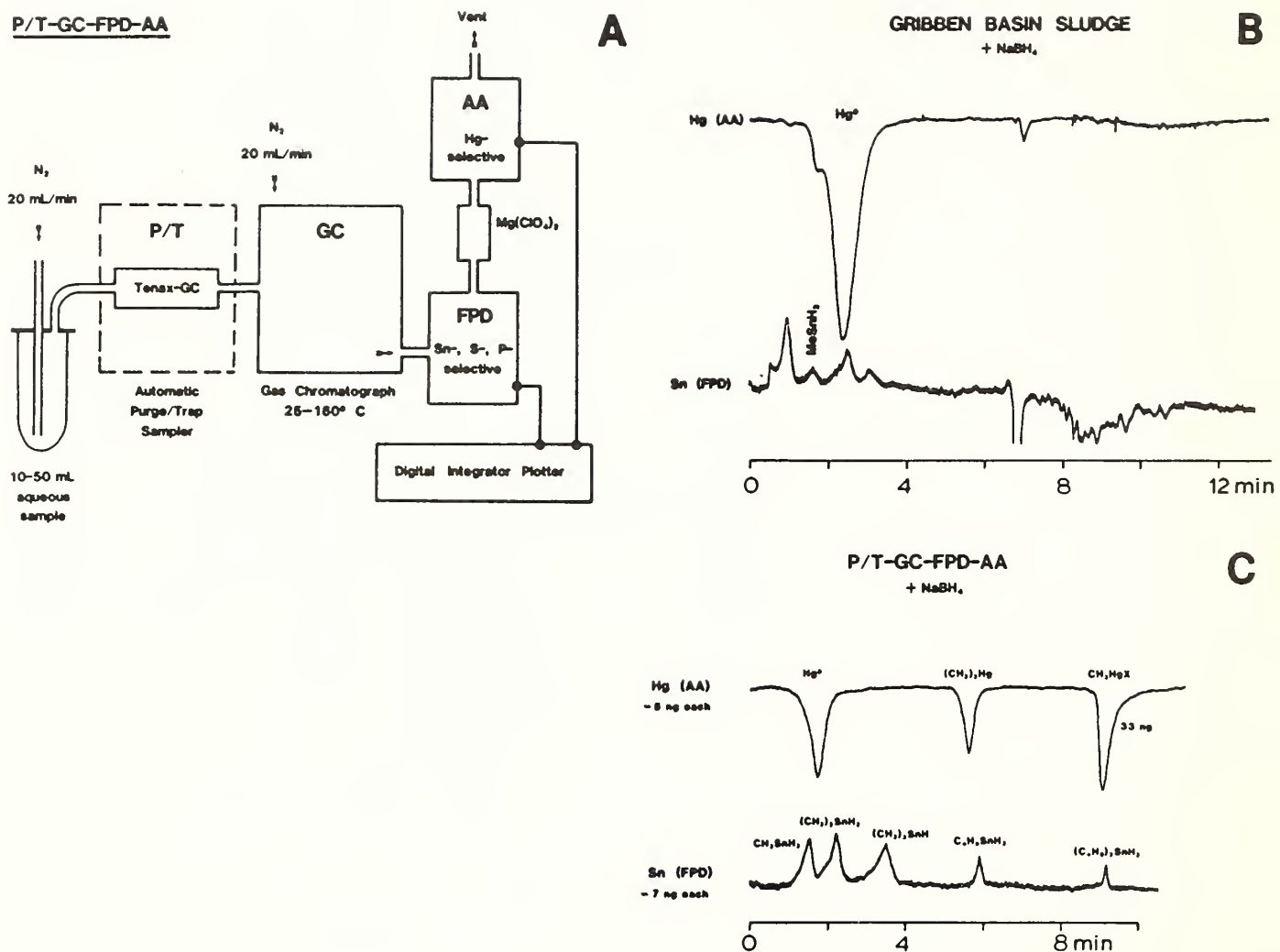


Figure 9 (A) Block diagram of purge and trap gas chromatography system employing tandem flame photometric (tin-selective) and atomic absorption (Hg-selective) detectors (P/T-GC-FPD-AA). (B) Detection of tin and mercury species in a polluted lake are shown in this chromatogram. (C) Authentic compounds in deionized water. Samples (10 mL) were treated with sodium borohydride to generate volatile mercury and tin species.

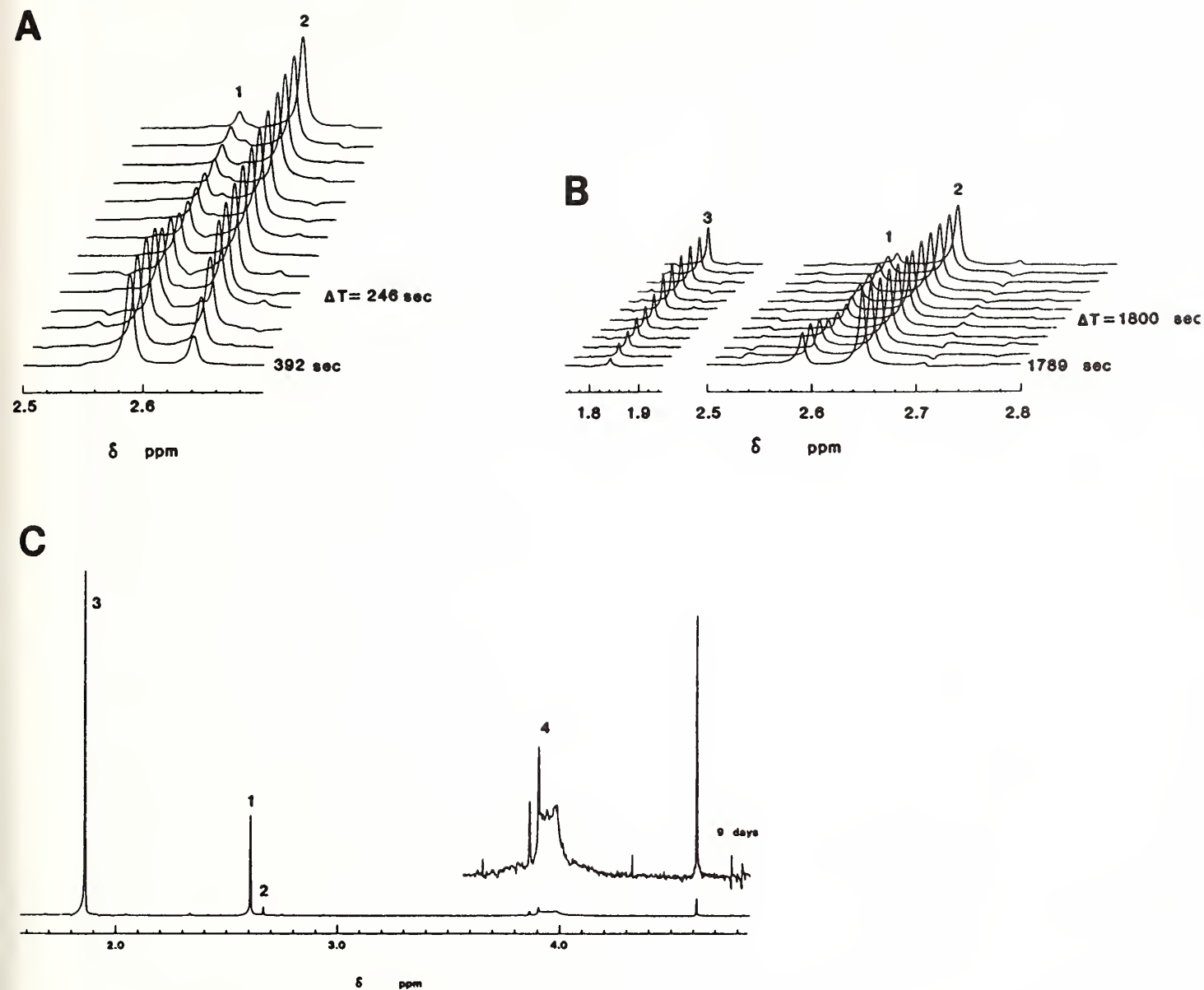


Figure 10 Proton NMR spectra of the reaction of CH_3I (1) with soluble Na_2S (A,B) and insoluble SnS (C) in D_2O . CH_3I (0.09 M) and Na_2S (0.045 M) react rapidly at 27 °C to form $(\text{CH}_3)_2\text{S}$; (2) shown in A. $(\text{CH}_3)_2\text{S}$ reacts with additional MeI to form $(\text{CH}_3)_3\text{S}^+$ ion; (3) shown in B. Reaction in B was run at ~ 4 °C with 0.09 M CH_3I and 0.02 M Na_2S . Heterogeneous reaction between SnS and CH_3I is shown, after nine days, in C. Production of a methyltin species (4) was indicated.

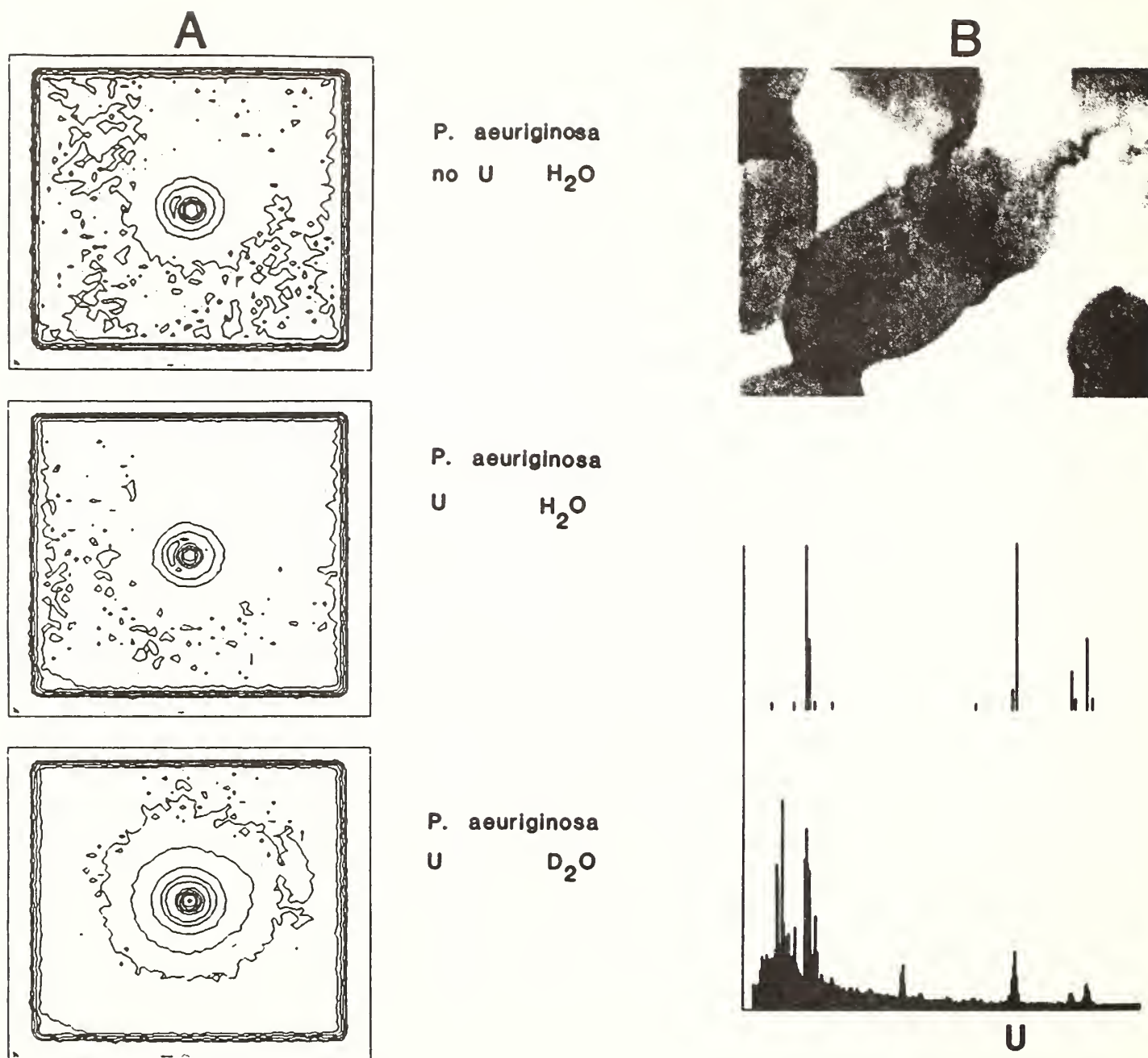


Figure 11 (A) Neutron scattering computer plots from cells of *Pseudomonas* ($\sim 10^{10} \text{ mL}^{-1}$) exposed to aqueous U and resuspended in H_2O or D_2O . Differences in scattering were noted in cells with U compared to cells without U. Cells resuspended in D_2O gave plots with improved signal to noise. (B) Confirmation that cells accumulated U was provided by transmission electron microscopy with energy dispersive X-ray microanalysis (TEM-EDAX).

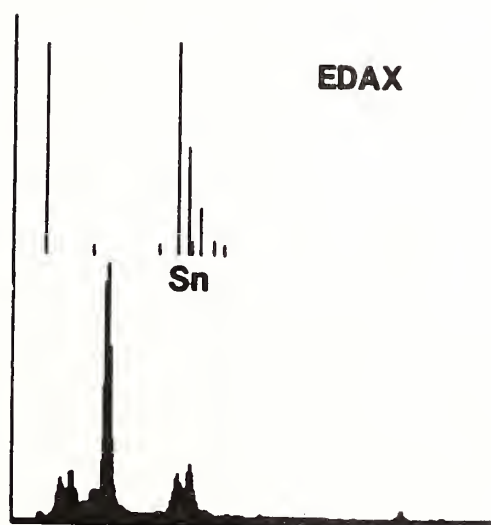
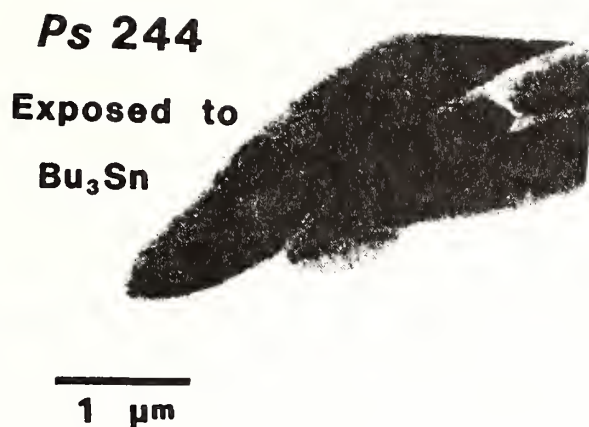


Figure 12 Results are shown from a rapid and simple technique for obtaining a TEM-EDAX spectrum from metal-accumulating bacteria. Cells of *Pseudomonas* strain 244 were exposed to 10 mg L⁻¹ tributyltin chloride for one hour, were washed several times in a buffer solution and were then adsorbed to carbon-coated nylon grids. Without further manipulation, the cells were examined and found to contain tin.

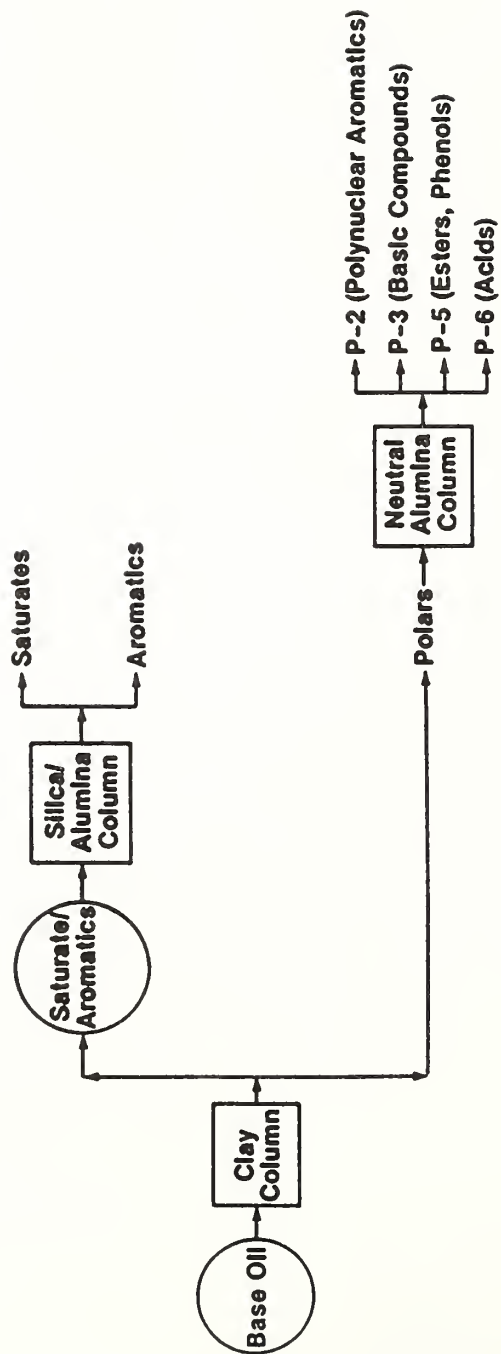


Figure 13 Separation Scheme of the Base Oil Into Fractions and Compound Classes

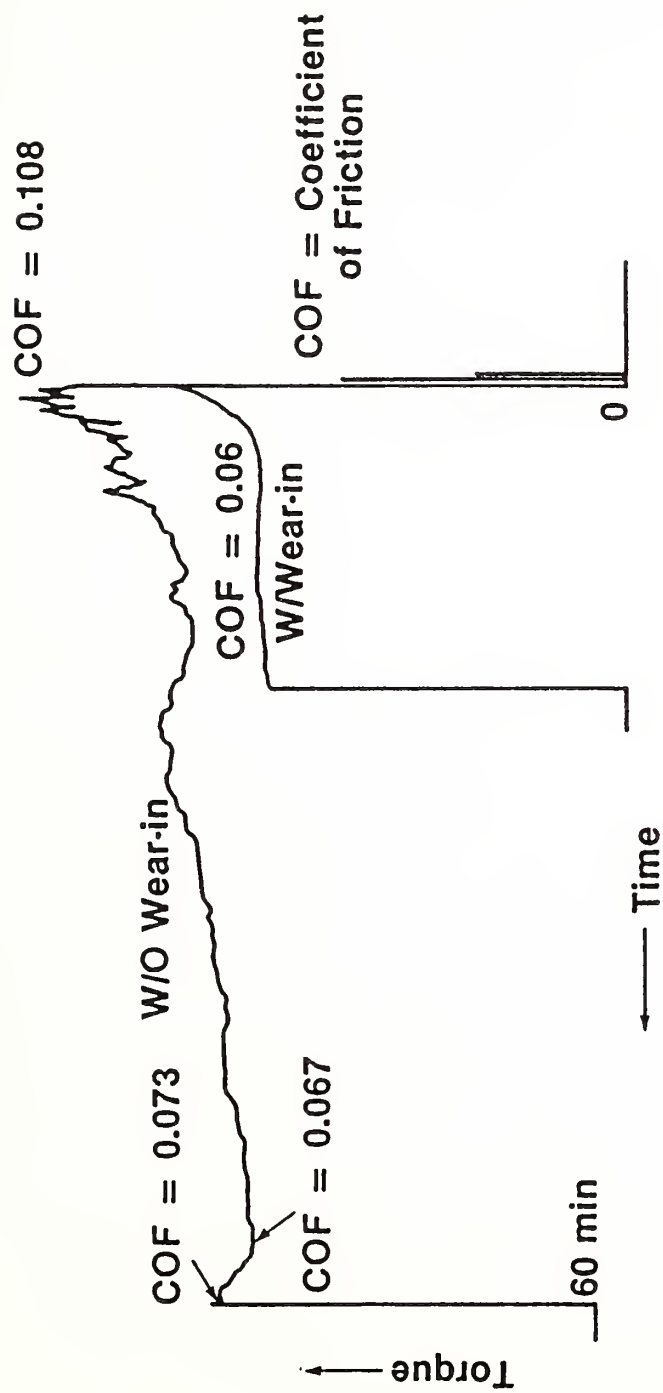


Figure 14 Effects of Wear-in Procedures on Frictional Torque

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5. INVITED TALKS

Laser Enhanced Ionization Spectrometry for Trace Metal Analysis
FACSS, Philadelphia, PA
G. C. Turk, G. J. Havrilla, P. K. Schenck, and J. C. Travis
September 1982

Current Research Activities in Tribochemistry at NBS
ASME Research Committee Meeting, NBS, Washington, DC
S. M. Hsu
October 1982

Discussion on the Base Oil Effects on Engine Performance
International Fuels and Lubricants Meeting, Society of Automotive
Engineers, Toronto, Canada
S. M. Hsu
October 1982

Discussion on the Effects of Temperatures on Simulated Valve Drain
Wear
ASME/ASLE Joint Meeting, Washington, DC
S. M. Hsu
October 1982

DSC and TGA Methods Applied to Fuel Instability
Conference on Storage Stability of Middle Distillate Fuels, Naval
Research Laboratory, Washington, DC
S. M. Hsu
October 1982

Energy Dispersive X-Ray Diffraction
Federal University do Rio Grande do Sol, Rio Grande do Sol, Brazil
S. Block
October 1982

The Heat of Fusion of Tungsten by Levitation Calorimetry
Containerless Processing Working Group Annual Meeting, Arlington, VA
D. W. Bonnell and J. L. Margrave
October 1982

High Pressure Studies of Materials
Federal University of Rio Grande do Sol, Rio Grande do Sol, Brazil
S. Block
October 1982

Interfacing Size Exclusion Chromatography and Graphite Furnace
Atomic Absorption for the Characterization of Organometallic Macromolecules
American Society for Testing and Materials, E-19 Annual Meeting,
New Orleans, LA
E. J. Parks and F. E. Brinckman
October 1982

Gravity Effects on Flame Inhibition
Reduced Gravity Combustion Science Working Group, NASA, Cleveland, OH
J. W. Hastie
January 1983

High Temperature Structural Reliability of Structural Ceramics
Seventh Annual Conference on Composites and Advanced Ceramic
Materials, American Ceramic Society, Cocoa Beach, FL
S. M. Wiederhorn and N. J. Tighe
January 1983

A Crack as a Crystalline Defect
Science Lecture, Sandia National Laboratories, Albuquerque, NM
E. R. Fuller, Jr.
February 1983

High Pressure Studies of Materials
University of Maryland, College Park, MD
S. Block
February 1983

Ion-Electron Dynamics in Flames
Oberlin College, Oberlin, OH
P. K. Schenck
February 1983

Ion-Electron Dynamics in Flames
Sohio Gas Corporate Research Laboratory, Cleveland, OH
P. K. Schenck
February 1983

NBS and the Optogalvanic Effect
Oberlin College, Oberlin, OH
P. K. Schenck
February 1983

Anaerobic Corrosion by Sulfate-Reducing Bacteria Due to a Highly
Reactive Volatile Phosphorous Compound
National Physical Laboratory, Teddington, London, England
W. P. Iverson and G. J. Olson
March 1983

Crystallographic and Magnetic Changes of $Y_6Mn_{23}D_{23}$ with Temperature
in a Neutron Diffraction Study
University of Missouri, Columbia, MO
K. Rhyne
March 1983

Effects of Agglomerates in Green Ceramics
NBS/NDE Review Panel, NBS, Washington, DC
T. Negas
March 1983

Ultratrace Chemical Speciation Techniques Applied to the Study of
Microbial Tin and Mercury Transformations
American Society for Microbiology, North Central Branch Meeting,
La Crosse, WI
G. J. Olson
October 1982

Experimental and Theoretical Activity Models for Slags and Related
Materials
Seventh Annual Conference on Materials for Coal Conversion and
Utilization, NBS, Washington, DC
J. W. Hastie, D. W. Bonnell, and E. R. Plante
November 1982

High Pressure Studies of Materials
University of Campinas, Brazil, Brazil
S. Block
November 1982

High Temperature Toughness of Silicon Carbide Materials in a
Controlled Gaseous Environmental
Seventh Annual Conference on Materials for Coal Conversion and
Utilization, NBS, Washington, DC
R. F. Krause, Jr., L. Chuck, and E. R. Fuller, Jr.
November 1982

The Influence of Electrostatic Forces on Crack Propagation in Glass
Martin Marietta Laboratories, Baltimore, MD
S. M. Wiederhorn
November 1982

NBS Recycled Oil Program
U.S. Army Mobility Equipment Research and Development Command, Fort
Belvoir, VA
S. M. Hsu
November 1982

The Reaction of Silicon Carbide with Product Gases of Coal Combustion
Seventh Annual Conference on Materials for Coal Conversion and
Utilization, NBS, Washington, DC
A. L. Dragoo and J. L. Waring
November 1982

Tectosilicates--New Data on Processing Physical and Electronic
Properties and Chemical Durability
Seventh Annual Conference on Materials for Coal Conversion and
Utilization, NBS, Washington, DC
L. P. Cook, C. K. Chiang, and T. Hahn
November 1982

Quality Control Methods for Re-refined Lubricants
ASTM Committee D-2 Meeting, Norfolk, VA
S. M. Hsu
December 1982

Enhanced Crack Blunting

Advanced Research Workshop on Strength of Glass, Armacao de Pera,
Algarve, Portugal

T. Michalske, E. R. Fuller, Jr., and T.-J. Chuang

March 1983

Environmentally Enhanced Crack Growth in Glasses

NATO Conference on Fracture of Glass, Algarve, Portugal

S. W. Freiman

March 1983

Extension of Simple Proof Testing Concepts

Advanced Research Workshop on Strength of Glass, Armacao de Pera,
Algarve, Portugal

E. R. Fuller, Jr. and S. M. Wiederhorn

March 1983

Fracture Mechanics Parameters for Glasses: Compilation and Correlation

NATO Conference on Fracture Glass, Algarve, Portugal

S. W. Freiman, J. B. Wachtman, Jr., and T. L. Baker

March 1983

Indentation: Deformation and Fracture Processes

NATO Conference on Strength of Glass, Algarve, Portugal

B. R. Lawn

March 1983

Kinetics of Elementary Fracture Processes

Advanced Research Workshop on Strength of Glass, Algarve, Portugal

E. R. Fuller, Jr.

March 1983

Materials and Processing Problems Associated with Sulfate-Reducing
Bacteria in Petroleum Recovery

American Chemical Society National Meeting, Seattle, WA

G. J. Olson, W. P. Iverson, and F. E. Brinckman

March 1983

Microbial Corrosion--An Overview

City of London Polytechnic, Calcutta House Prescint, London
England

W. P. Iverson

March 1983

Strength of Glass: A Controlled Flaw Study

NATO Conference on Strength of Glass, Algarve, Portugal

B. R. Lawn and D. B. Marshall

March 1983

Surface Flaws in Glass

NATO Conference on Strength of Glass, Algarve, Portugal

D. B. Marshall and B. R. Lawn

March 1983

The Chemical Nature of Lubricating Film in Wear Contacts
International Conference on Wear of Materials, Reston, VA
S. M. Hsu
April 1983

Fracture Toughness of Polymer Concrete Materials Using Various
Chevron-Notched Configurations
ASTM Symposium on Chevron-Notched Specimens: Testing and Stress
Analysis, Louisville, KY
R. F. Krause, Jr. and E. R. Fuller, Jr.
April 1983

Keynote Address: Phase Equilibria and Crystal Chemistry of High
Frequency Dielectrics
American Ceramic Society Annual Meeting, Chicago, IL
R. S. Roth
April 1983

Relationship Between Oxidation Stability and Thermal Stability of
Lubricants
Conference on Tribology in the Eighties, NASA Lewis, Cleveland, OH
S. M. Hsu
April 1983

Reliability of Ceramics for Heat Engines
Cornell University, Materials Seminar, Ithaca, NY
N. J. Tighe
April 1983

Short and Long Range Magnetic Ordering of $Y_6(Fe_{1-x}Mn_x)_{23}$ Compounds
Using Neutron Scattering Techniques
Sixteenth Rare Earth Research Conference, Tallahassee, FL
K. Hardman-Rhyne
April 1983

ASTM/NBS Basestock Consistency Study: A Hot Bed for Multivariant
Analysis
Statistical Engineering Division Seminar, NBS, Washington, DC
S. M. Hsu
May 1983

A Theoretical Analysis of Temperature Dependent Electron Impact
Fragmentation
31st American Association for Mass Spectrometry, Boston, MA
D. W. Bonnell and J. W. Hastie
May 1983

The Computer Aided Revolution in X-ray Power Diffraction
Fifth Australian School/Conf. on X-ray Analysis, Melbourne, Australia
C. R. Hubbard
May 1983

Continuous Phase Transitions in Zirconium Titanate
University of Pennsylvania, Philadelphia, PA
A. E. McHale
May 1983

Experimental and Modeling Studies of Vaporization and Phase Equilibria
for Coal Slag and Other Silicate Systems
Symposium on High Temperature Materials Chemistry, Electrochemical
Society 1983 Annual Meeting, San Francisco, CA
J. W. Hastie, D. W. Bonnell, and E. R. Plante
May 1983

Experimental and Modeling Studies of Vaporization and Phase Equilibria
for Coal Slag and Other Silicate Systems
Sandia National Laboratories, Livermore, CA
J. W. Hastie
May 1983

Knudsen Effusion and Transpiration Mass Spectrometry Studies of
Halogen-Alkali Silicate Interactions
31st American Association for Mass Spectrometry, Boston, MA
E. R. Plante, J. W. Hastie, and D. W. Bonnell
May 1983

Manual Search/Match Methods Workshop
Fifth Australian School/Conf. on X-Ray Analysis, Melbourne, Australia
C. R. Hubbard
May 1983

Phase Equilibria Modeling of Complex Oxide Solid, Liquid, Vapor
Systems
Los Alamos National Laboratory, Los Alamos, NM
J. W. Hastie
May 1983

Pressure Calibration in Transpiration Mass Spectrometry
Workshop on Mass Spectral Pressure Calibration
31st Annual American Society for Mass Spectroscopy Meeting,
Boston, MA
D. W. Bonnell
May 1983

Progress in XRD Quantitative Analysis
Fifth Australian School/Conf. On X-Ray Analysis, Melbourne, Australia
C. R. Hubbard
May 1983

Reliability of Structural Ceramics
Material Science Seminar, Oak Ridge National Laboratory, Oak Ridge, TN
S. M. Wiederhorn and E. R. Fuller, Jr.
May 1983

Studies of Ceramic Materials Using Small Angle Neutron Scattering
Techniques

Alfred University Seminar, Alfred, NY

K. Hardman-Rhyne

May 1983

Thermodynamic and Structural Inferences from Activity Models in
Silicates

International Symposium on Structure and Bonding of Non-crystalline
Solids, Reston, VA

J. W. Hastie

May 1983

Time Dependent Failure

U.S.-China Seminar on Microstructure and Mechanical Properties of
Ceramics, Shanghai, China

S. M. Wiederhorn

May 1983

Transpiration Mass Spectrometric Analysis of Liquid KOH Vaporization
Symposium on High Temperature Materials Chemistry, Electrochemical
Society 1983 Annual Meeting, San Francisco, CA

J. W. Hastie, K. F. Zmbov, and D. W. Bonnell

May 1983

Crack Tip Reversibility

NBS Conference on Crack Tip Structure and Process, NBS, Washington, DC

B. J. Hockey

June 1983

Effects of Crack Tip Chemistry on Crack Growth in Glasses and
Ceramics

NBS Conference on Crack Tip Structure and Processes, Washington, DC

S. W. Freiman

June 1983

The Environmental Chemistry Inorganic of Main Group Elements

U.S.--Italy Workshop on Environmental Chemistry, San Miniato, Italy

F. E. Brinckman

June 1983

On the Thermodynamic Extension Force of Growing Creep Microcrack

Conference on Crack Tip Structure and Processes, NBS, Washington, DC

T.-J. Chuang

June 1983

Optogalvanic Spectroscopy at NBS

Centre d'Etudes Nucleaires Fontenay aux Roses (CNRS), Aussois,
France

P. K. Schenck

June 1983

Physical Mechanisms of Laser Enhanced Ionization
CNRS Conference on Optogalvanic Spectroscopy and Its Applications,
Aussois, France
P. K. Schenck, J. C. Travis, and G. C. Turk
June 1983

Short and Long Range Magnetic Ordering of $Y_6(Fe_{1-x})Mn_n)_{23}$ Compounds
Using Neutron Scattering Techniques
Seminar at Louis Niel Laboratory, CNRS, Grenoble, France
K. Hardman-Rhyne
June 1983

U.S. Army/NBS Engine Test Program
ASTM Joint B and P Meeting, Kansas City, MO
S. M. Hsu
June 1983

Chemistry of CdS Materials Containing Cl Which Exhibit Magnetic and
Electrical Anomalies
IX AIRAPT Conf., Albany, NY
S. Block
July 1983

Speciation and Molecular Topology as Predictors of Microbial Uptake
of Metals
Gordon Research Conference on Microbial Degradation, Brewster
Academy, Wolfsboro, NH
F. E. Brinckman
July 1983

Anaerobic Corrosion of Iron and Steel--A New Mechanism
Third International Symposium on Microbial Ecology, East Lansing, MI
W. P. Iverson and G. J. Olson
August 1983

Environmental Organotin Chemistry
Fourth International Conference on the Organometallic and Coordination
Chemistry of Germanium, Tin, and Lead, McGill University, Montreal,
Quebec, Canada
F. E. Brinckman
August 1983

Microstructure and Electrical Properties of Ceria-Based Ceramic
Electrolytes
Conference High Temperature Solid Oxide Electrolytes, Brookhaven
National Laboratory, Upton, NY
A. L. Dragoo and C. K. Chiang
August 1983

Quantitative XRD Workshop
Denver X-Ray Conference, Snowmass, CO
C. R. Hubbard
August 1983

6. RECENT SEMINARS

The Division maintains an active Seminar Program in which lectures by distinguished visitors on scientific topics of interest to the Division are supplemented by presentations of current work by Division scientists. In FY83, the Division sponsored almost three seminars per month, of which 87 percent were presented by scientists from outside NBS.

Crystal Structure Predictions from Computer Simulations

A. N. Cormack

University College London, London, England

October 1982

Structural Investigations of Rare Earth and Alkali Ion Apatites

I. Mayer

Hebrew University, Jerusalem, Israel

October 1982

Chemomechanical Weakening of Geologic Materials in Surface Active Aqueous Environments

J. D. Dunning

Indiana University, Bloomington, IN

October 1982

Auger and Photoelectron Line Energy Relationships in Aluminum-Oxygen and Silicon-Oxygen Compounds

D. A. Passoja

Union Carbide Corp., Tarrytown, NY

October 1982

Precision Machining, Finishing and Polishing of Optical and Magnetic Materials

Y. Namba

Osaka University, Osaka, Japan

November 1982

Correlations Between Chemical Structure and Biological Activity of Organotin Compounds

R. Laughlin

University of California, Oakland, CA

November 1982

Shear Faults and Crack Initiation in Glass

T. P. Dabbs

National Bureau of Standards, Gaithersburg, MD

November 1982

Measuring Microbial Transformations and Accumulation of Metals: Implications for Biotechnology

F. E. Brinckman

National Bureau of Standards, Gaithersburg, MD

December 1982

Adsorption of Microorganisms to Surfaces
G. A. McFeters
Montana State University, Bozeman, MT
December 1982

Structural Reliability of Ceramic Materials
Staff of the Mechanical Properties Group
National Bureau of Standards, Gaithersburg, MD
March 1983

The Fracture Mechanics of Concrete and Rock: Testing and Numerical Modeling
A. R. Ingraffea
Cornell University, Ithaca, NY
March 1983

Computer Simulations as an Aid to Structure Determination
A. N. Cormack
University College London, London, England
April 1983

Computer Modeling and Neutron Scattering Studies of Disorder in Fluorite-Structured Crystals
C. R. A. Catlow
University College London, London, England
April 1983

Crystal Growth and Vaporization of Indium Telluride
R. Santandrea
Max Planck Institute for Solid State Research, Stuttgart, Federal Republic of Germany
April 1983

Role of Interfaces on Delayed Failure of Glass--Glass-Ceramic Composites with Implications Regarding Proof Testing Procedures
A. V. Virkar
University of Utah, Salt Lake City, UT
April 1983

Grain Growth and Morphology of BaTiO_3 and Ferrite Ceramics
M. Drofenik
Jozef Stefan Institut, Ljubljana, Yugoslavia
May 1983

Problems and Limitations in Small Angle Neutron Scattering
E. Case
University of California, Berkeley, CA
May 1983

Strength and Fatigue of Optical Fibers
W. J. Duncan
British Telecommunications Research Laboratory, Ipswich, England
May 1983

Microstructure Development in Technical Ceramics
Lecture 1: Sintering, Grain Growth, and Firing of Technical Ceramics
Lecture 2: Sintering Additives
R. J. Brook
University of Leeds, Leeds, England
May 1983

Application of Ceramic Materials to Diesel Engines
G. L. Starr
Cummins Engine Company, Inc., Columbus, IN
May 1983

The Fractal Character of Ceramic and Metal Fracture
D. E. Passoja
Union Carbide Corp., Tarrytown, NY
B. B. Mandelbrot
IBM Corp., Yorktown Heights, NY
May 1983

Crystal Chemistry: A Tool for Interpreting Large Angle X-Ray
Scattering
J. Galy
Laboratoire de Chimie de Coordination, Toulouse, France
May 1983

Sintering and Microstructure Development in Ceramics
D. Kolar
University of Ljubljana, Ljubljana, Yugoslavia
May 1983

Evaluation of Friction and Wear of Lubricants and Materials
S. M. Hsu
National Bureau of Standards, Gaithersburg, MD
May 1983

Laser Annealing of Thin-Film Optical Waveguides
H. E. Jackson
University of Cincinnati, Cincinnati, OH
May 1983

Magnetite Precipitation by Bacteria
R. P. Blakemore
University of New Hampshire, Durham, NH
June 1983

Physics of Sintering of Silicon
W. S. Coblenz
Naval Research Laboratory, Washington, DC
June 1983

Cluster Variation Model for Calculation of Melt Free Energies
R. Kikuchi
Hughes Research Laboratories, Malibu, CA
June 1983

Phase Relations and Properties via Molecular Dynamics

R. G. Munro

National Bureau of Standards, Gaithersburg, MD

June 1983

Toughening of Ceramics: Development of Ceramic Composites

R. W. Rice

U.S. Naval Research Laboratory, Washington, DC

June 1983

Ceramics in Japan (Highlights of 1983 Visit)

J. J. Mecholsky

Sandia National Laboratories, Albuquerque, NM

August 1983

Industrial Chemistry and Applications of Organotins

P. J. Smith

International Tin Research Institute, London, England

August 1983

Magnesium Diffusion in Basic Oxygen Furnace (BOF) Refractories

C. E. Semler

Ohio State University, Columbus, OH

August 1983

7. PROFESSIONAL SOCIETY AND STANDARDS COMMITTEE PARTICIPATION

American Ceramic Society

Committee on Glass Standards Classification and Nomenclature

M. J. Cellarosi, Chairman

Committee on Government Liaison

M. J. Cellarosi, Member

Committee on Publications

Subcommittee on "Phase Diagrams for Ceramists"

R. S. Roth, Chairman

Committee on Reference Materials

W. K. Haller, Member

Coordinating Committee

S. J. Schneider, Member

Editorial Committee--Basic Science Division

S. M. Wiederhorn, Subchairman

Executive Committee--Basic Science Division

N. J. Tighe

Forum Committee--Basic Science Division

N. J. Tighe

Research Committee (Phase Diagrams)

L. P. Cook, Chairman

J. W. Hastie, Member

Resource Committee

S. J. Schneider, Member

Sosman Lecture Committee

N. J. Tighe, Member

American Chemical Society

Inorganic Materials Division--Nonmenclature Committee

T. D. Coyle, Chairman

Nomenclature Committee

T. D. Coyle, Member

American National Standards Institute (ANSI)

Committee N43--Equipment for Ionizing Radiation

S. Block, Member

Committee 43.1--Safety Standards for X-ray Diffraction and
Fluorescence Analysis Equipment

S. Block, Chairman

F. A. Mauer, Secretary

American Petroleum Institute

Task Group on Cements for Geothermal Wells

E. R. Fuller, Jr., Member

R. F. Krause, Jr., Member

American Physical Society

Editorial Board, Review of Scientific Instruments

P. K. Schenck, Member

American Society for Testing and Materials

- C8: Refractories
 - Awards Committee
 - S. J. Schneider, Chairman
 - Conditions of Tests
 - S. J. Schneider, Member
 - Specifications
 - S. J. Schneider, Member
- C9: Concrete and Concrete Aggregates
 - C. R. Robbins, Member
- C14: Glass and Glass Products
 - M. J. Cellarosi, Chairman
 - C14.01: Nomenclature of Glass and Glass Products
 - M. J. Cellarosi, Chairman
 - C14.03: Chemical Properties of Glass
 - W. K. Haller, Member
 - C14.04: Physical and Mechanical Properties of Glass
 - M. J. Cellarosi, Member
 - D. J. Cronin, Member
 - C14.08: Flat Glass
 - M. J. Cellarosi, Member
- C18: Natural Building Stones
 - C. R. Robbins, Member
 - C18.034: Sandstone
 - C. R. Robbins, Member
 - C18.07: Environmental Properties, Behavior and Cleaning
 - C. R. Robbins, Member
- C-21: Committee Ceramic Whitewares
 - S. M. Wiederhorn, Member
- D2: Petroleum Products and Lubricants
 - S. M. Hsu, Member
 - D2.0B: Automotive Lubricants
 - S. M. Hsu, Member
 - B-1: Passenger Car Oils
 - B-2: Diesel and Truck Oils
 - D2.0P: Recycled Petroleum Products
 - S. M. Hsu, Chairman
 - P-0: Advisory
 - P-1: Automotive Lubricants
 - P-2: Used Oils and Basestocks
 - P-3: Fuel Oils
 - P-4: Industrial and Hydraulic Oils
 - P-6: Miscellaneous Products
 - P-7: Editorial
 - D2.04: Hydrocarbon Analysis
 - P. T. Pei, Member
 - 4A: Preparation of Standard Hydrocarbon Blends
 - 4B: Methods by Chemical Means
 - 4C: Liquid Phase Chromatography
 - 4D: Properties by Physical Means

- 4F: Absorption Spectroscopy Method
- 4G: Manual on Hydrocarbon Type Analysis
- 4K: Correlative Methods
- 4.01: Gas Chromatography
- 4M: Mass Spectroscopy Methods
- D2.06: Analysis of Lubricants
 - S. M. Hsu, Member
 - P. T. Pei, Member
- D2.07: Flow Properties
 - S. J. Weeks, Member
- D2.09: Oxidation
 - C. S. Ku, Member
- 9D: Lubricants and Hydraulic Fluids
- 9F: Used Oil Oxidation/Nitration
- 9G: Additive Response of Base Oils
- E19: Chromatography
 - E. J. Parks, Member
- E20: Temperature
 - S. J. Schneider, Member
- Subcommittee E24.07 on Fracture of Non-Metals
 - S. W. Freiman, Chairman
 - E. R. Fuller, Jr., Member
- Task Group E24.07.01 Fracture Toughness Testing of Concretes and Rocks
 - E. R. Fuller, Jr., Member
- Task Group E24.07.02 Double-Torsion Technique
 - E. R. Fuller, Jr., Member
- E34: Occupational Health and Safety Aspects of Materials, Physical and Biological Agents
 - F. E. Brinckman, Member
- E38: Resource Recovery
 - M. J. Cellarosi, Member
 - C. R. Robbins, Member
- E38.06.03: Fly Ash in Construction Materials
 - C. R. Robbins, Member
- E44: Solar Energy Conversion
 - F1.02: Laser
 - A. Feldman, Member
- E47: Biological Effects and Environmental Fate
 - F. E. Brinckman, Member
 - G. J. Olson, Member

American Society of Automotive Engineers
 Fuels and Lubricant Committee
 S. M. Hsu, Member

American Society of Lubrication Engineers
 Annual Meeting Program Committee
 S. M. Hsu

Committee on Wear

S. M. Hsu, Vice President

R. S. Gates, Member

Lubrication Fundamentals Committee

S. M. Hsu, Member

R. S. Gates, Member

C. S. Ku, Member

Technical Coordinator for Conservation and Recycling Committee

S. M. Hsu

Technical Coordinator for Metal-working Committee

S. M. Hsu

Technical Coordinator for Mining Committee

S. M. Hsu

Technical Coordinator for Seals Committee

S. M. Hsu

American Society of Mechanical Engineers

Ceramics Committee

N. J. Tighe, Member

Gas Turbine Division

N. J. Tighe, Member

High Temperature Science

Editorial Advisory Board

J. W. Hastie, Member

IEEE

International Symposium on Applications of Ferroelectrics

H. P. R. Frederikse, Local Chairman

InterAmerican Conferences on Materials Technology

Executive Committee

S. J. Schneider, Member

International Commission on Glass

Subcommittee A.II: Durability and Analysis

W. K. Haller, Member

Subcommittee VIII: Standard Reference Glasses

W. K. Haller, Vice Chairman

U.S. Representative

W. K. Haller

Subcommittee VI A

S. M. Wiederhorn, Chairman

International Union of Crystallography

Commission on Crystallography at Controlled Pressures and Temperatures

G. J. Piermarini, Member

International Union of Pure and Applied Chemistry

Commission II-2: Nomenclature of Inorganic Materials

T. D. Coyle, Titular Member, Secretary

Commission II-3: High Temperature Chemistry Refractory Materials
J. W. Hastie, Associate Member
Interdivisional Committee on Nomenclature and Symbols
T. D. Coyle, Titular Member
Conferences on Refractories for Energy Applications
Planning and Program Committees
S. J. Schneider, Member

JCPDS-International Centre for Diffraction Data
S. Block, Member
C. R. Hubbard, Member and Vice-Chairman
Board of Directors
Technical Committee
Long-range Planning Committee
Ceramics Subcommittee
Data Collection and Analysis Subcommittee
Data Base Subcommittee
Search/Match Methods Subcommittee

Joint ASTM-ASLE Committee on Industrial Lubricants
S. M. Hsu, Member
Subsection 1: Falex Wear Test Development
Subsection 2: Four-ball Wear Test Development
Subsection 8: Friction Test Development

Joint Committee of Atomic and Molecular Physical Data
NMR Subcommittee
R. B. Johannesen, Chairman

Joint Electron Devices Engineering Councils
X-ray and Implosion TV Standards Committee
M. J. Cellarosi, Member

Journal of Physical and Chemical Reference Data
Editorial Board
H. M. Ondik, Member

The Metals Properties Council, Inc.
Subcommittee 9--Coal Conversion
S. J. Schneider, Member

National Materials Advisory Board
Committee on Reliability of Ceramics for Heat Engine Applications
S. M. Wiederhorn, Member
Committee on Mineral Resources Technology
S. J. Schneider, Liaison Representative

National Materials Review Board (MRB) for Nuclear Waste
Data and Testing Procedures Committee
T. Negas, Member
H. P. R. Frederiske, Member

National Research Council
Committee on High Temperature Science and Technology
J. W. Hastie, Chairman
Committee on Recommendations for U.S. Army Basic Scientific
Research
S. M. Wiederhorn, Member

Optical Society of America
Committee on Standards
A. Feldman, Member

8. SPONSORED CONFERENCES, SPECIAL REPORTS, BOOKS AND SRMs

Sponsored Conferences

Seventh Annual Conference on Materials for Coal Conversion and Utilization
Joint with Department of Energy, Electric Power Research Institute and Gas Research Institute
S. J. Schneider, Organizer
November 1982

Symposium on the Periodic Table in Chemical Education
Joint with ACS Committee on Nomenclature, Division of Chemical Information and Division of Inorganic Chemistry
T. D. Coyle, Organizer
March 1983

Special Reports

Chuang, T.-J. On the energy-release rate associated with diffusional crack growth. Nat. Bur. Stand. (U.S.) NBSIR 82-2628; Report to the Department of Energy; 1982.

Cronin, D. J.; Blackburn, D. H. Haller, W. K. Property composition relationships of ytterbium containing borate glasses. Final report to Lawrence Livermore National Laboratories. December 1982.

Parks, E. J.; Johannesen, R. B.; Brinckman, F. B. Advances in the SEC characterization of organometallic copolymers and copolymerization: desorption of charged species by injected dilute acetic acid. Nat. Bur. Stand. (U.S.) NBSIR 82-2577; Report to the David Taylor Naval Ship R & D Center; 1982.

Robbins, C. R. Fossil fuel technology waste sampling and characterization program. Task III, physical and chemical characterization. Quarterly report to Department of Energy, Laramie Energy Technology Center. January 1982.

Robbins, C. R. Fossil fuel technology waste sampling and characterization program. Task III, physical and chemical characterization. Quarterly report to Department of Energy, Laramie Energy Technology Center. May 1982.

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Schneider, S. J.; Fuller, Jr., E. R.; Fields, R. J.; Chuang, T.-J.; Krause, R.; Dragoo, A.; Munro, R. G. Quarterly progress reports to Department of Energy sponsor for high temperature applications of structural ceramics. September 1982, December 1982, March 1983, June 1983.

Schneider, S. J.; Ondik, H. M.; Christ, B. W.; Perloff, A.; Tighe, N. J.; McDaniel, C. L.; Wiederhorn, S. M. Quarterly progress reports to Department of Energy sponsor for materials research on the clean utilization of coal. September 1982, December 1982, March 1983, June 1983.

Blair, W. R.; Parks, E. J.; Brinckman, F. E. Characterization of controlled release dynamics and identification of released species from OMP impregnated wood pilings. Nat. Bur. Stand. (U.S.) NBSIR 83-2733; Report to the Naval Civil Engineering Laboratory; 1983.

DeVoe, J. R.; Travis, J. C.; Turk, G. C.; Weeks, S. J. Laser enhanced ionization in flames. Nat. Bur. Stand. (U.S.) NBSIR 83-2668; Report to Environmental Protection Agency; 1983.

Feldman, A.; Malitson, I. Recommended reference materials for realization of physicochemical properties: refractive index. Report to International Union of Pure and Applied Chemistry; 1983.

Hastie, J. W.; Plante, E. R.; Bonnell, D. W. Vaporization of simulated nuclear waste glass. Nat. Bur. Stand. (U.S.) NBSIR 83-2731; Report to E. I. Dupont; 1983.

Iverson, W. P.; Olson, G. J. The mechanism of anaerobic microbial corrosion. Nat. Bur. Stand. (U.S.) NBSIR 83-2738; Report to the Office of Naval Research; 1983.

Negas, T. Development of materials and processing for luminescent standards. Final report to U.S. Postal Service Laboratories. February 1983.

Robbins, C. R.; Kruger, J. Determination of the deterioration of bronze plaques. Final report to U.S. National Park Service, April 1983.

Stephenson, G. B.; Bienenstock, A. I.; Haller, W. K. Dynamic SAXS investigation of early-stage phase separation in amorphous systems. Stanford Research Laboratory, Yearly Activity Report; 1983.

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C. S. Ku and S. M. Hsu, 1983

9. RESEARCH ASSOCIATE AND GUEST WORKER PROGRAMS

Industrial Research Associates

Chemical and Biodegradation Processes Group--F. E. Brinckman, Group Leader

Name: T. F. Degnan; Affiliation: Mobil Research and Development Corporation; NBS Sponsor: F. E. Brinckman; Technical Activity: molecular characterization and monitoring of arsenic catalyst poisons in candidate processes for shale oils-measurement technology.

Ceramic Sciences Group--T. Negas, Group Leader

Joint Committee for X-ray Powder Diffraction Standards (JCPDS)--International Centre for Diffraction Data. Staff at NBS: M. E. Morris--Director, E. H. Evans, N. Pyrros, Research Associate, B. Paretzkin, H. F. McMurdie, H. S. Parker, D. Gladhill, T. Olert, C. Wingo; R. Snyder--Consultant, Alfred University, Department of Ceramic Engineering; Sponsor: C. R. Hubbard and T. Negas.

This non-profit corporation functions in cooperation with the American Ceramic Society, the American Crystallographic Association, the American Society for Testing and Materials, the Clay Minerals Society, the Institute of Physics, the Mineralogical Society of America, the Mineralogical Society of Great Britain and Ireland, the National Association of Corrosion Engineers, and the Societe Francaise de Mineralogie et de Cristallographie. JCPDS produces the Powder Diffraction File (PDF) which is a continuing compilation of diffraction patterns gathered from numerous sources. Over 80 industries in Fortune 500 and over 1200 other private, government, and academic organizations purchase the data. NBS contributes new or improved data to the PDF as well as XRD techniques and SRMS, especially applicable to the processing and quality control of ceramic and metal alloy materials.

Glass and Optical Materials Group--W. Haller, Group Leader

Name: A. C. Siefert; Affiliation: approximately 20 glass companies through ASTM; NBS Sponsors: G. A. Uriano and M. J. Cellarosi; Technical Activity: the program establishes priority listing of SRMs of interest to glass industry and coordinates SRM-material procurements and work done outside of NBS.

Chemical Stability and Tribology Group--S. M. Hsu, Group Leader

Name: S. C. Hsu; Affiliation: Chinese Petroleum Corporation; NBS Sponsor: S. M. Hsu; Technical Activity: the program synthesizes organic compounds relating to the additive response characteristics of lubricants--measurement technology.

Name: S. Lin; Affiliation: Chinese Petroleum Corporation;
NBS Sponsor: S. M. Hsu; Technical Activity: the program
characterizes lubricant composition with respect to oxidation
stability and wear--measurement technology.

Industrial Guest Workers

Ceramic Sciences Group--T. Negas, Group Leader

Name: R. J. Cava; Affiliation: Bell Labs, Murray Hill, NJ;
NBS Sponsor: R. S. Roth; Technical Activity: research on
structure/properties of ionic conducting materials.

Name: L. P. Domingues, Research and Development Director;
Affiliation: Trans-Tech, Inc., Division of Alpha Industries;
NBS Sponsor: T. Negas; Technical Activity: research deals
with the characterization of ceramic powders, compacts, and
densified microstructures for dielectric ceramics.

Glass and Optical Materials Group--W. Haller, Group Leader

Names: K.-H. Lee and Y.-C. Hwang; Affiliation: Precision
Instrument Development Center, Taiwan; NBS Sponsor: D. M. Sanders;
Technical Activity: this work deals with the development of
techniques to prepare and measure the mechanical properties of
unsupported thin films.

Mechanical Properties Group--S. M. Wiederhorn

Name: D. Greenspan; Affiliation: LARC International; NBS Sponsor:
S. W. Freiman; Technical Activity: using infrared spectroscopy
to study the chemical reactions that occur during crack growth in
glass.

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